



Faculty of Sciences

Department of Physics and Astronomy

APPLICATION OF MgO-EA/DYE SURFACE MODIFIED Ni-ZnO ETL NANORODS ON
HTL FREE CARBON ELECTRODE PEROVSKITE SOLAR CELLS

by

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BSc Physics (UoB)

A Thesis submitted to the Faculty of Sciences in Fulfilment of the Requirements for the Award
of the Degree of Master of Science in Physics of BIUST

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May 2024

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ACKNOWLEDGEMENTS

Firstly, I would like to thank the Almighty God who gave me life, pursued me, gave me wisdom and directed my every step to this day. He showered me with His grace and empowered me to be where I am today.

Secondly, I would like to thank my parents who raised me and made sure I become what I am today. They gave me the freedom to pursue my interests with hope that I will become the best version of myself. In the process they gave me all the necessary love and support to ensure that I achieve my personal goals.

Thirdly, I would like to thank my supervisors who introduced me to field of material science, guided me and helped me to grow and establish myself in academics. They are responsible for my academic growth and my achievements in the academic diaspora.

Fourthly, I extend my thanks to my colleagues and friends who encouraged me daily and supported me making sure that I do not lag behind in the pursuit of this milestone. All in the knowledge that in times of graduation it will be a merry time for all.

Lastly I would like to thank the technicians whom we laboured together in the heat of the day in sample fabrication and data acquisition. Even though let down by machines several times they pulled through to make sure that I get the desired results

DEDICATION

I would like to dedicate this work to my parents, Collen Thobega and Khumoetsile Thobega not forgetting my aunt Pauline Thobega as they have selflessly laboured to support me morally and financially.

LIST OF PUBLICATION

Published from this work

1. **M. Thobega**, K. Maabong Tau, K. Lefatshe, C. Muiva “Study of structural, optical and electrical properties of Nickel doped ZnO (Ni–ZnO) nanorods grown by chemical bath deposition” *Physica B: Condensed Matter*, 2023

Other publications

1. K. Maabong, C. M. Muiva, P. Monowe, T. S. Sathiaraj, M. Hopkins, L. Nguyen, K. Malungwa and **M. Thobega**, Natural Pigments as Photosensitizers for Dye-Sensitized Solar Cells with TiO₂ Thin Films, *international journal of renewable energy research*, Vol.5, No.1, 2015

ABSTRACT

Chemical bath deposition method was used to grow Nickel doped ZnO (Ni-ZnO) thin films on a seed layer grown using the conventional spray pyrolysis method. Structural, optical and electrical properties were studied at different doping levels of Ni (0, 2, 4, 6 and 8 %) to the molar concentration of ZnO. All samples exhibited a highly defined (002) peak indicating a strong hexagonal crystal structure orientation. Samples with low levels of the dopant indicated lower mean roughness values. The grain size decreased from 167 nm for pure ZnO to lowest of 79 nm at 2% Ni concentration. Optical and electrical properties showed an optimum value at 2% Ni concentration. The 2% Ni-ZnO film was then used to fabricate a perovskite solar cell of the order FTO/Ni-ZnO/MgO-EA/Dye/Perovskite/Carbon/FTO. XRD analysis was performed to confirm the Ni-ZnO/MgO structure of the ETL. The dye treated FTO/Ni-ZnO/MgO layers were evaluated for their optical properties. The untreated ethanolamine (EA) layer showed higher transmittance followed by rosebengal (RB) and brilliant Black BN (BBBN) treated layers respectively. The transmittance was observed to be on the range 40% to 60% within the visible spectral range. The obtained band gap values for the dye treated samples were found to be in the range 3.05-3.06 (eV). Electrical properties of FTO/Ni-ZnO/MgO-EA/Dye were studied. High conductivity measurements were obtained from the BBBN treated sample at 1.26×10^3 ($1/\Omega\text{cm}$) followed by EA at 1.03×10^3 ($1/\Omega\text{cm}$) and RB at 9.9×10^2 ($1/\Omega\text{cm}$). From the I-V properties of the solar cells it was observed that RB treated layer produced higher efficiency of 0.0056% compared to the untreated EA (0.0043%) and BBBN (0.001%) respectively. The RB dye increased the solar cell V_{oc} from 0.090V (EA) to 0.12V while the BBBN drastically reduced the V_{oc} to 0.02 V. However, the BBBN-treated cell maintained higher I_{sc} current of 0.193 mA in the proximity of untreated EA which produced 0.203 mA compared to RB which reduced I_{sc} to 0.134 mA. Among the three samples, RB-treated sample produced higher fill factor (FF) ratio of 0.53 which corresponds to higher photoelectric power conversion rate of 0.00560 mW/cm^2 followed by untreated EA with FF (0.37) corresponding to 0.00430 mW/cm^2 and lastly BBBN with FF of 0.40 corresponding to 0.00119 mW/cm^2 . In overall the RB treated solar cell showed better results compared to the other samples.

Table of Contents

<i>DECLARATION REGARDING THE WORK AND COPYRIGHT</i>	<i>ii</i>
<i>CERTIFICATION</i>	<i>i</i>
<i>ACKNOWLEDGEMENTS</i>	<i>2</i>
<i>DEDICATION</i>	<i>3</i>
<i>LIST OF PUBLICATION</i>	<i>4</i>
<i>ABSTRACT</i>	<i>5</i>
<i>LIST OF FIGURES</i>	<i>9</i>
<i>LIST OF TABLES</i>	<i>10</i>
<i>LIST OF ABBREVIATIONS</i>	<i>11</i>
CHAPTER 1.....	13
INTRODUCTION.....	13
1.1 Overview	13
1.2 Research Statement	14
1.3 Aims and Objectives	15
CHAPTER 2.....	16
LITERATURE REVIEW.....	16
2.1 Perovskite Solar Cells.....	16
2.2 Solar Cell Physics.....	17
2.2.1 How Solar Cells Function	17
2.2.2 Thin-Film Solar Cells	18
2.2.3 Organic Solar Cells.....	18
2.2.4 Perovskite Solar Cells:.....	19
2.3 The solar cell's mechanism of operation:.....	19
2.3.1 Sunlight Absorption.....	19
2.3.2 Charge Separation	19
2.4 P-N junction, I-V properties	20
2.5 Perovskite Solar Cell Development.....	22
2.6 Perovskite architecture	23

2.6.1	<i>TCO Layer (Transparent Conducting Oxide)</i>	25
2.6.2	<i>Perovskite Layer</i>	25
2.6.3	<i>Charge Transport Layer</i>	25
2.6.4	<i>Regular and Inverted Planar Setup</i>	25
CHAPTER 3.....		28
METHODOLOGY AND DEPOSITION TECHNIQUES		28
3.1	Deposition methods.....	28
3.1.1	Low-Cost ZnO Thin Film Deposition Techniques	29
3.1.1.1	<i>Chemical Bath Deposition (CBD)</i>	29
3.1.1.2	<i>Spray Pyrolysis Deposition (SPD)</i>	30
3.1.1.3	<i>Sol-Gel Technique</i>	31
3.1.2	High-Cost Techniques for ZnO Thin Film Deposition.....	31
3.1.2.1	<i>Pulsed Laser Deposition (PLD)</i>	31
3.1.2.2	<i>Molecular Beam Epitaxy (MBE)</i>	32
3.1.2.3	<i>Metal Organic Chemical Vapor Deposition of (MOCVD)</i>	33
3.2	Deposition of the perovskite layer.....	33
3.3	HTL/ Conductive /layer deposition	35
3.4	EXPERIMENTAL PROCEDURE.....	36
3.4.1	<i>Synthesis of Ni-ZnO Seed Layer</i>	36
3.4.2	<i>Synthesis of Ni-ZnO Nano-rods</i>	36
3.4.3	<i>Deposition of MgO Layer</i>	37
3.4.4	<i>Preparation and Deposition of Dyes</i>	37
3.4.5	<i>Deposition of The Perovskite Layer/Carbon Layer</i>	37
3.4.6	<i>Characterization of Thin Films</i>	39
CHAPTER 4.....		41
RESULTS AND ANALYSIS		41
4.1	ANALYSIS OF Ni-ZnO THINFILMS	41

4.1.1 STRUCTURAL PROPERTIES	41
4.1.1.1 XRD analysis.....	41
4.1.1.2 RAMAN analysis.....	43
4.1.2 MORPHOLOGICAL analysis.....	44
4.1.3 OPTICAL PROPERTIES.....	48
4.1.4 ELECTRICAL PROPERTIES.....	51
4.2 ANALYSIS OF THE PROPERTIES OF THE PEROVSKITE SOLAR.....	53
4.2.1 STRUCTURAL ANALYSIS	53
4.2.1.1 XRD analysis.....	53
4.2.2 OPTICAL ANALYSIS	54
4.2.3 ELECTRICAL STUDIES	57
4.2.3.1 I-V Characteristics of Solar Cells	57
4.3 CONCLUSIONS AND RECOMMENDATIONS	61
4.3.1 CONCLUSIONS	61
4.3.2 RECOMMENDATIONS	63
REFERENCES.....	64

LIST OF FIGURES

FIGURE 1: Pie chart showing energy consumption by fuel: source; Worldenergydata.org.....	13
FIGURE 2: A diagram showing carbon free PSC and carbon-based PSC structure.....	16
FIGURE 3: A diagram showing solar cell structure: source; www.tumblr.com/hacksscience/.....	18
FIGURE 4: A diagram showing forward and reverse bias P-N junction: source; http://electronicstrainer.blogspot.com/	20
FIGURE 5: A diagram showing solar cell parameters [30].....	21
FIGURE 6: Planar Perovskite solar cell structure	25
FIGURE 7: Normal and Inverted perovskite solar cell structure: source; www.zsw- bw.de/en/research/photovoltaics/topics/perovskite-solar-cells.html	26
FIGURE 8: A schematic diagram showing the CBD process	29
FIGURE 9: A photograph of spray pyrolysis setup.....	30
FIGURE 10: A diagram of spin coating process [63]	34
FIGURE 11: A schematic diagram of doctor blade method [71]	35
FIGURE 12: A photograph of HHV TF500 machine	38
FIGURE 13: A photograph showing samples after the deposition of the perovskite layer for MgO- EA, MgO-EA/RB and MgO-EA/BBBN	38
FIGURE 14: A photograph showing solar samples after the deposition of carbon paste.....	39
FIGURE 15: A circuit diagram used in solar cell testing	40
FIGURE 16: XRD patterns for $Ni_x - ZnO$ where $x = (0, 2, 4, 6, 8 \%)$, (a) showing the intensity from 2theta 10-80 and (b) zoomed portion of the (002) peaks.	41
FIGURE 17: Raman spectra for $Ni_x - ZnO$ where $x = (0, 2, 4, 6, 8 \%)$	44
FIGURE 18: FESEM micrographs of pure ZnO and 2, 4, 6 and 8% Ni doped ZnO, EDX spectrum for $Ni_x - ZnO$	45
FIGURE 19: 3D AFM images showing surface morphology of the thin films	45
FIGURE 20: Histograms showing grain size distribution for pure ZnO and 2, 4, 6 and 8% Ni doped ZnO	47
FIGURE 21: (a) Transmittance spectra of the prepared $Ni_x - ZnO$ $x = (0, 2, 4, 6$ and $8 \%)$. thin films. (b) Tauc plot of $(\alpha h\nu)^2$ against. (c) $\ln(\alpha)$ against $h\nu$ for the prepared $Ni_x - ZnO$ thin films. For the Urbach plots, plot a scatter and fit with the line of best fit	49
FIGURE 22: Variation of resistivity and conductivity for $Ni_x - ZnO$ $x = (0, 2, 4, 6$ and $8 \%)$ thin films	51
FIGURE 23: XRD pattern for FTO glass substrate coated with layers of Ni-ZnO and MgO-EA	53

FIGURE 24: A SEM image for as-prepared layer FTO/Ni-ZnO/MgO-EA	54
FIGURE 25: Optical transmittance (a) and absorbance (b) for different dye treatments RB and BBN55	
FIGURE 26: Graph showing band gap energies (E_g) for EA, RB, BBBN, treated FTO/Ni-ZnO/MgO-EA layers.....	56
FIGURE 27: A schematic representation of the fabricate solar cell device.....	58
FIGURE 28: I-V characteristics for the fabricated solar cells (a) I-V curves for all fabricated samples	
(b) Ethanolamine treated sample (c) Rose Bengal treated sample (d) Blackburn BN treated sample	.59

LIST OF TABLES

Table 1: Calculated structural specifications for the prepared undoped ZnO and Ni _x -ZnO thin films.	42
Table 2: Surface morphological characteristics of Ni _x -ZnO x = (0, 2, 4, 6 and 8 %)	46
Table 3: Estimated bandgap energy and Urbach energy for Ni _x -ZnO	50
Table 4: Measured electrical parameters for Ni _x -ZnO x = (0, 2, 4, 6 and 8 %) thin films.....	51
Table 5: Estimated band gap energies for EA, RB and BBBN treated samples	56
Table 6: Electrical parameters of dye treated FTO/Ni:ZnO/MgO-EA	57
Table 7: I-V parameters of the fabricated samples.....	60

LIST OF ABBRIVIATIONS

2-MTHF	2-Methyltetrahydrofuran
ALD	Atomic Layer Deposition
CaTiO₃	Calcium Titanium Trioxide
CBD	Chemical Bath Deposition
CuI	Copper Iodide
DMF	Dimethyl Formamide
DMSO	Dimethyl Sulfoxide
DSSCs	Dye-Sensitized Solar Cells
EA	Ethanolamine
EBE	Electron Beam Evaporation
EPFL	Ecole Polytechnique Federale de Lausanne
ET	Electron transport
ETL	Electron Transport Layer
HT	Hole transport
HTL	Hole Transport Layer
I_{max}	Maximum current
I_{sc}	Short circuit current
LEDs	Light Emitting Diodes
MAI	Methyl Ammonium Iodide
MAPbI₃	Methyl Ammonium Lead Iodide
MgO	Magnesium Oxide
MOCVD	Metal Organic Chemical Vapour Deposition
OLEDs	Organic Light Emitting Diodes
PbI₂	Lead Iodide
PCE	Power Conversion Efficiency
PEDOT:PSS	Poly(3,4-Ethylene Dioxythiophene)
PLD	Pulsed Laser Deposition
P_{max}	Maximum power in Watts
PSCs	Perovskite Solar Cells
PVK	Poly(N-Vinyl Carbazole)
RFMs	Radio-Frequency Magnetron Sputtering
SPD	Spray Pyrolysis Deposition

SPIRO-OMETAD

2,2',7,7'-Tetrakis [N,N-di(4-methoxyphenyl) amino]-9,9'-spirobifluorene

TBA

Tert-Butyl Alcohol

TCOs

Transparent Conducting Oxide

 $V_{\max}$

Maximum voltage

 V_{oc}

Open Circuit Voltage

XRD

X-ray diffraction

ZnO

Zinc Oxide

CHAPTER 1

INTRODUCTION

1.1 Overview

The past few decades have seen a sharp rise in the world's energy consumption as a result of population development, industrialization, and urbanization [1]. This has led to increased use of fossil fuels as the main sources of energy. These fossil fuels include coal, oil, and natural gas, but their use has detrimental effects on the environment and society, such as air pollution, climate change, and geopolitical conflicts [2]. In order to handle these issues, growing interest has been shown in direction of creating renewable energy sources such as solar, wind, hydro, and geothermal power. Among these renewable energy sources solar energy is regarded as one of the most promising due to its availability, accessibility, and minimal negative effects on the ecosystem [3] [4] [5]. Despite efforts to increase the use of solar, generation of electricity by solar is still estimated to 1% with oil and coal leading the way at 30.4% and 25.9% respectively as shown in FIGURE 1.

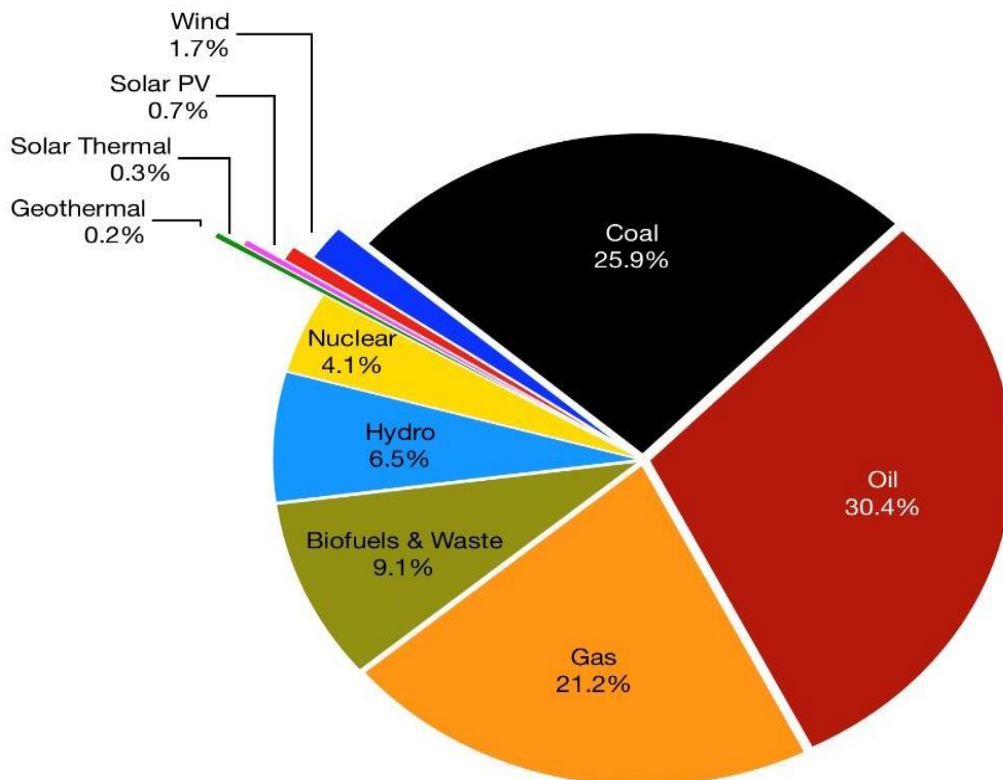


FIGURE 1: Pie chart showing energy consumption by fuel: source;Worldenergydata.org

Recent developments in solar energy conversion technology have made perovskite solar cells a hopeful venture. Based on hybrid organic-inorganic perovskite materials, these cells are highly efficient at absorbing a wide variety of light wavelengths and converting them into electricity [6] [7]. Perovskite solar cells have made significant strides in terms of efficiency and stability, with lifetimes of several years and record efficiencies surpassing 25% [8] [9][8] [10]. Perovskite solar cells have a large potential to meet the world's energy needs. The International Energy Agency (IEA) estimates that by 2050, solar energy could supply up to 16% of the world's electricity needs, making it the biggest source of electricity [1]. Perovskite solar cells have the ability to aid in this transition by offering high-efficiency, low-cost technology that can be widely used.

1.2 Research statement

Despite the potential for high performance, the stability and durability of the perovskite solar cell components, particularly the electron transport (ET) and the hole transport (HT), present a significant challenge to perovskite solar cells technology [2] [11]. The study of ZnO ETL as a replacement for the commonly used TiO_2 in perovskite solar cells is a quite interesting venture. In most cases the ZnO has proven to be a worthy rival to TiO_2 as it matches TiO_2 performances. However, ZnO easily suffers from defects such as easy degradation, oxidations and reacts easily with the perovskite layer, therefore, the quest to modify ZnO layer into a robust and sustainable material has been an interesting research field. One of the potential solutions to this problem is surface modification. The electronic structure, wettability, and adhesion of the ETL and HTL materials can be enhanced by altering their surfaces, which will enhance charge transport and lessen degradation. It has been noted that using ethanolamine (EA), a typical organic molecule, to modify the surface of metal oxide surfaces can increase the surfaces' wettability and adhesion in the setting of perovskite solar cells. Due to its high electron mobility and excellent stability, magnesium oxide (MgO) is also a frequently used metal oxide material for the ETL modification. The hydrophobic nature of MgO surfaces, however, is known to restrict the adhesion of perovskite layers, resulting in decreased performance and stability of the solar cells [18] [122].

Researchers have looked into using EA-modified MgO surfaces in perovskite solar cells as a way to overcome restriction. It has been observed that EA functionalization of the MgO surface enhances the perovskite layers' wettability and adhesion, leading to improved overall solar cells' performance and durability. The use of dyes in conjunction with MgO surfaces that have undergone EA modification has been investigated as a means to enhance the performance of perovskite solar cells even more. Dye molecules can boost light absorbance and increase the effectiveness of electron injection, which will increase photocurrent and boost the performance of perovskite solar cells. Recent research has also focused on optimizing charge carrier dynamics in perovskite solar cells, which could further improve their efficiency and stability [2] [12] [13].

1.3 Aims and Objectives

In this thesis, we examine the use of Ni-ZnO ETL nanorods with a MgO-EA surface modification on carbon electrode perovskite solar cells without HTL. Through modifying the ETL's surface properties and investigating the potential of dye molecules to improve performance, this research seeks to increase the stability and efficiency of perovskite solar cells. We will analyse the characteristics of the MgO-EA surface and how dye molecules interact with it, as well as the efficiency of the resulting perovskite solar cells.

Specific objectives of this study are to:

1. Fabricate Nickel doped Zinc oxide nanorods using seed layer method and Chemical bath deposition.
2. Characterise the thin films and determine the best performing samples to act as a HTL
3. Modify the Ni-ZnO layer using MgO-EA/dye, analyse and determine the best sample
4. Fabricate and characterize a solar cell of structure (FTO/Ni-ZnO/MgO-EA/Dye/Perovskite/Carbon/FTO).

CHAPTER 2

LITERATURE REVIEW

2.1 Perovskite Solar Cells

Due to their cheap cost, high efficiency, and simplicity of production, perovskite solar cells (PSCs) have emerged as a very promising replacement for conventional silicon-based solar cells [13]. The choice of appropriate electrode materials for effective charge transfer and collection, though, is one of the PSC's difficulties [14].

Metal oxide electron transport layers (ETLs) like TiO_2 , SnO_2 , or ZnO and hole-transporting layers (HTLs) like Spiro-OMeTAD or PEDOT:PSS have historically been used in PSCs [15]. PSCs with carbon electrodes, on the other hand, have drawn more attention as a result of their potential to outperform conventional HTLs in terms of affordability, stability, and environmental kindness [16]. FIGURE 2 shows planar structure of perovskite solar cell with HTL and without HTL.

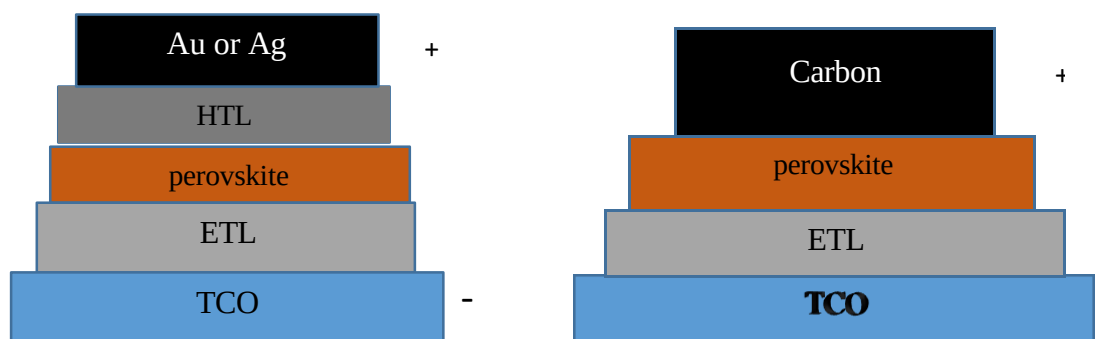


FIGURE 2: A diagram showing Carbon free PSC and Carbon based PSC structure

However, carbon electrodes perform less in PSCs than traditional HTLs due to their lower conductivity and poorer hole transport characteristics. In order to overcome this difficulty, scientists have investigated numerous approaches to alter the ETL's surface with functional

groups or nanoparticles, which can enhance the electron transport characteristics and lower recombination. Utilizing Ni-ZnO ETL nanorods with MGO-EA surface modifications in PSCs with carbon electrodes devoid of HTL is one such method [17]. The MGO-EA modification can enhance electron transport and lessen recombination at the carbon/ETL interface, which enhances device efficiency all around.

The application of Ni-ZnO ETL nanorods with MGO-EA surface modifications in PSCs with carbon electrodes has been examined in several investigations. J. Zhang et al [18] have found out that the MGO-EA modification can boost device performance by raising the fill factor and lowering the cell's series resistance [13] [14] [15] [16] [17]. According to a Y. Xiong et al, [19] the MGO-EA modification can increase the PSC's stability by lessening the degradation brought on by contact with oxygen and moisture [19]. Various electrode materials and modifications in PSCs were investigated. Researchers have investigated the use of electrodes made of graphene in PSCs, which can provide high conductivity and advantageous electron transport characteristics [20]. Others have investigated using metal nanoparticles or functionalized carbon nanotubes as anode materials or surface enhancers in PSCs [21] [16].

2.2 Solar Cell Physics

2.2.1 *How solar cells function*

The process of turning solar energy into electrical power using semiconductor materials is known as photovoltaics. The photovoltaic effect, which happens when light photons strike a semiconductor material and excite its electrons to a higher energy level, underlies this technology. This voltage differential can be used to produce electricity. The schematic diagram of a solar cell is shown in FIGURE 3.

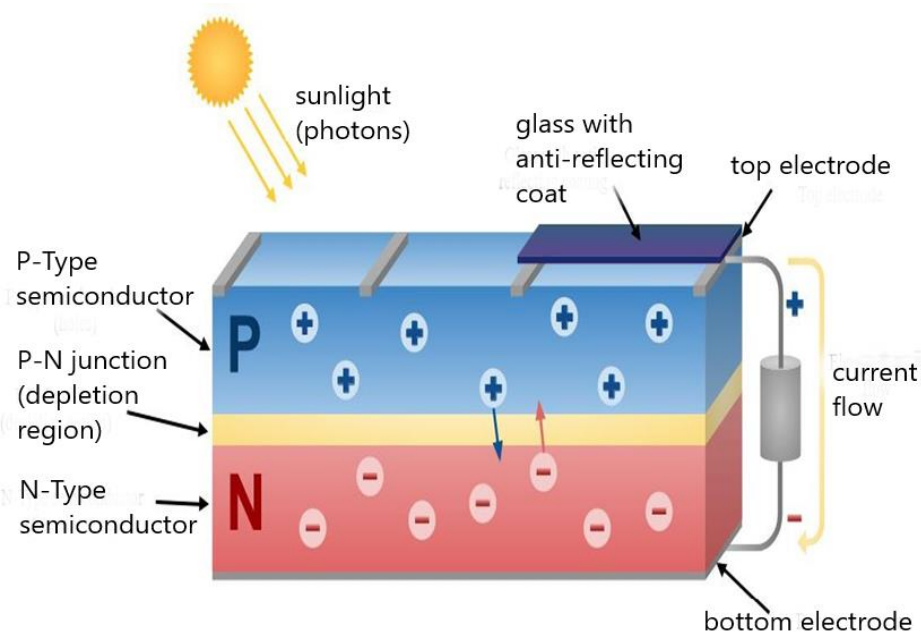


FIGURE 3: A diagram showing solar cell structure: source; www.tumblr.com/hacksscience/

Solar cells come in compositional variances, each with a unique composition and operation. The most popular solar cells on the market right now are those made of crystalline silicon. They are extremely effective at converting sunlight into energy and are made of highly pure silicon in monocrystalline and polycrystalline varieties.

2.2.2 Thin-Film Solar Cells:

Amorphous silicon, cadmium telluride, or copper indium gallium selenide are just a few examples of the semiconductor materials used to make these solar cells. Despite being less effective, they are more affordable to produce than crystalline silicon solar cells.

2.2.3 Organic Solar Cells:

Solar cells that are composed of organic materials, such as polymers or small molecules, are known as organic solar cells. Although they can be made flexible and are less expensive to make than silicon solar cells, their efficiency is still quite low.

2.2.4 Perovskite Solar Cells:

These solar cells are constructed from a unique kind of organic-inorganic substance known as perovskite. Due to their cheap cost and high efficiency, perovskite solar cells have seen a sharp rise in efficiency in recent years and have the potential to play a significant role in the solar market.

2.3 The solar cell's mechanism of operation:

2.3.1 Sunlight absorption

Sunlight absorption is the first stage of a solar cell's functioning. This is accomplished by using a semiconductor substance, like silicon, which is made to absorb solar photons, producing electron-hole couples. A photon excites an electron in a semiconductor substance to a higher conduction band level when it is absorbed by the material, leaving a positively charged "hole" behind. The result of this mechanism is an electron-hole pair [22] [23] [24] [25] [26].

2.3.2 Charge separation

In order to produce an electric current, the electron-hole pair produced in stage 2 needs to be split apart. A solar cell generates electron-hole pairs by absorbing sunlight, separating the charges, gathering the charges at various electrodes, and then allowing an electric current to travel through an external circuit. The p-type and n-type areas of the semiconductor material are joined to form a junction in order to accomplish this. The positively charged hole and the negatively charged electron are separated by an electric field produced by the connection. Electrodes on either side of the junction gather the charge after the electron and hole have been separated. On the n-type side of the junction, an electrode made of metal collects the electrons, while on the p-type side, an anode made of metal collects the holes. The resulting flow of electrical current can be used to power electrical equipment. The amount of sunlight a solar cell can receive, the effectiveness of charge separation and collection, and the effectiveness of converting the electricity produced into usable power are all factors that affect a solar cell's efficiency [26] [27] [28].

2.4 P-N junction, I-V properties

The connection between the applied voltage across the junction and the resulting current flow through the junction is referred to as the I-V characteristics of a P-N junction [29]. As shown in FIGURE 4 the depletion region shrinks when a voltage (V_a) is applied across a P-N junction in the forward bias direction and this shrinkage connects the positive terminal of the voltage source to the p-type material and the negative terminal to the n-type material. This makes it easier for charge carriers to pass across the junction. As a consequence, the current flow increases quickly with the voltage applied. According to a study conducted by the National Institute of Standards and Technology, the amount of energy being used in the process is what makes it so unique as the applied voltage is proportional to the difference between the Fermi energy in the n-type and p-type quasi-neutral regions [30].

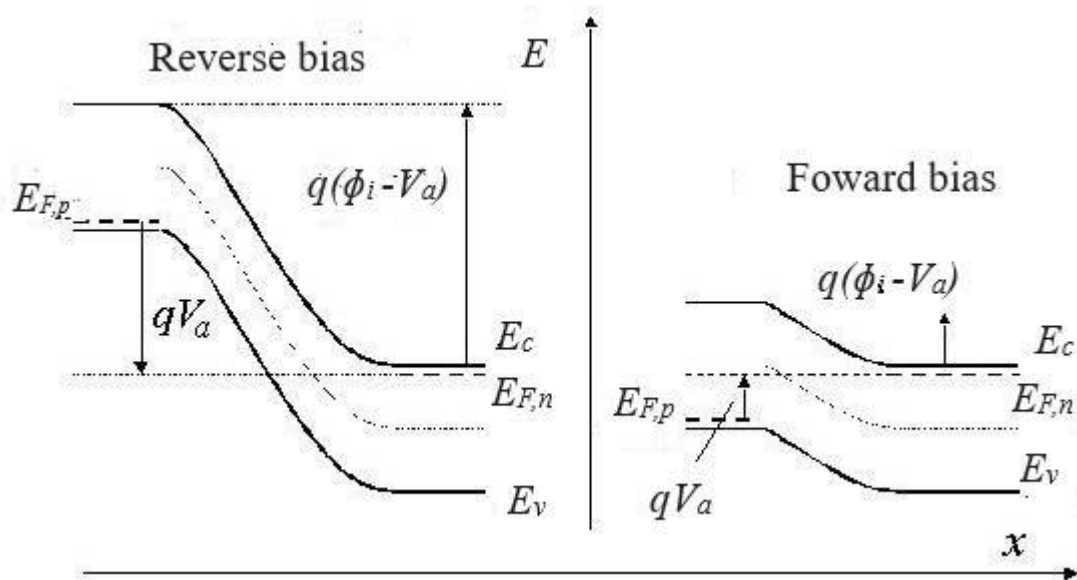


FIGURE 4: A diagram showing forward and reverse bias P-N junction: source; <http://electronicstrainer.blogspot.com/>:

The depletion area widens in the reverse bias direction, which connects the positive terminal of the voltage source to the n-type material and the negative terminal to the p-type material, making it more challenging for charge carriers to flow across the junction. As a consequence,

very low current flow is produced, which gradually increases with applied voltage up until a voltage threshold known as the breakdown voltage is reached. The depletion region collapses

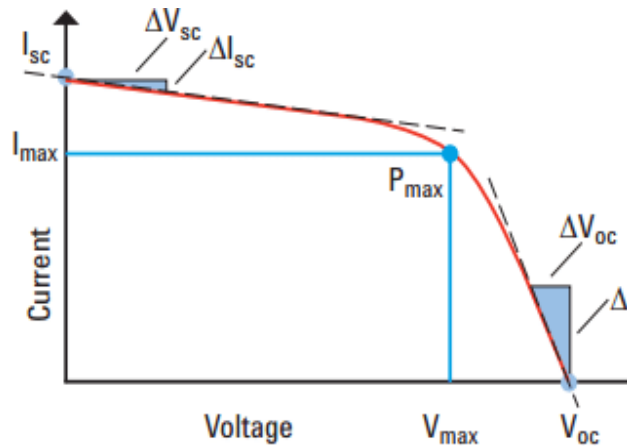


FIGURE 5:A diagram showing solar cell parameters [30]

at this voltage, enabling a sizable current to flow through the junction and possibly harm the device.

Efficiency (η) is the most crucial factor in a solar cell and is usually expressed as a percentage. It is defined as the ratio of the maximum output to the solar incident power [31]. The formula for efficiency is

$$\eta = \frac{P_{max}}{P_{in}} * 100\% \dots\dots\dots 1$$

, where P_{max} denotes the solar cell's maximum power production and P_{in} denotes the sun's incident power.

A solar cell's ability to convert incident light into electrical electricity is indicated by its fill factor [32]. Its formula is the highest power output divided by the product of the short-circuit current (I_{sc}) and the open-circuit voltage (V_{oc}). The fill factor is calculated using the following

$$FF = \frac{P_{max}}{(V_{oc} * I_{sc})} \dots\dots\dots 2$$

The maximum voltage that a solar cell can produce when there is no load attached to it is known as open-circuit voltage (V_{oc}). It serves as a gauge for the amount of energy that a solar cell is capable of producing. The equation for open-circuit voltage is given by

$$V_{oc} = \frac{kT}{q} \ln \frac{N_a N_d}{n_i^2} \dots\dots\dots 3$$

where k is the Boltzmann constant, T is the temperature, q is the electron charge, N_a and N_d are the doping concentrations of the p-type and n-type regions of the solar cell, respectively, and n_i is the intrinsic carrier concentration of the semiconductor material.

When the output is short-circuited the solar cell produce a current known as the short-circuit current and is calculated using the formula.

$$I_{sc} = \frac{q A n_s FF}{1000 V_t} \dots\dots\dots 4$$

and

$$I_{sc} = \frac{qA}{\tau} \dots\dots\dots 5$$

where q is the elementary charge of an electron (1.602×10^{-19} C), A is the surface area of the solar cell in (m^2), n_s is the number of solar cells connected in series, FF is the fill factor of the solar cell, which is a measure of how effectively the cell converts incident light into electrical power (typically between 0.5 and 0.8), V_t is the thermal voltage of the cell, which depends on the material properties and temperature of the cell, and τ is the average lifetime of the charge carriers in the semiconductor material [18] [33].

These are some of the most significant parameters, though there are many others that can be used to characterize the performance of a solar cell.

2.5 Perovskite Solar Cell Development

The discovery of dye-sensitized solar cells (DSSCs) in the 1990s led to the creation of perovskite solar cells (PSCs) [34]. In DSSCs, electron-hole pairs are created by a dye molecule's absorption of sunlight. A semiconductor material separates and collects these electron-hole pairs to create energy. Although DSSCs had the potential to be inexpensive and

extremely effective, they had a number of drawbacks, such as bad stability and a low absorption efficiency.

A perovskite material called methyl ammonium lead iodide (MAPbI_3) was used to create the first perovskite solar cell, which was described in 2009 by researchers at the École Polytechnique Fédérale de Lausanne (EPFL) in Switzerland [35]. Even though the device only had a 3.8% power conversion efficiency (PCE), it showed the promise of perovskite materials for photovoltaic applications.

The following few years saw researchers working to optimise the materials, device structures, and fabrication methods in order to increase the performance of PSCs. PSCs with PCEs over 10% were attained by 2012, and PSCs with PCEs over 22% were attained by 2016 [36]. The distinctive qualities of perovskite materials, such as their high absorption coefficients, extended carrier lifetimes, and tunable bandgaps, contributed to the quick advancement of PSC development.

The use of lead in the perovskite material raised toxicity concerns, which needed to be addressed, and PSCs also had poor stability. They also required better device architectures and fabrication techniques.

Researchers have made major strides in tackling these issues in recent years. For instance, they have created novel perovskite substances like mixed-cation perovskites and tin-based perovskites that are less toxic and more stable [37]. They have also looked into novel device architectures, like tandem cells and perovskite-silicon hybrid cells, that could help PSCs become even more effective and stable [36].

PSCs are currently one of the most hopeful photovoltaic technologies, with a 2020 PCE world record of 25.5% [38]. They have the potential to be inexpensive, portable, and extremely effective, which makes them perfect for a variety of uses, from portable electronics to large-scale power production. Before they can be widely used, however, more study is required to enhance PSCs' stability, scalability, and environmental "friendliness."

2.6 Perovskite architecture

The chemical formula ABX_3 describes the perovskite structure, a particular sort of crystal structure in which A and B are cations and X is an anion. The mineral perovskite, which has

the same crystal structure as the structure, is called after it. The A cation is frequently an organic or alkali metal, the B cation is frequently a metal like lead or tin, and the X anion is frequently a halide like iodine or bromide. Due to its distinct electronic characteristics, including its high charge carrier mobility, low exciton binding energy, and tunable bandgap, the perovskite structure has become well recognised [39].

German mineralogist Gustav Rose first identified the perovskite structure in the perovskite (CaTiO_3) mineral in the Ural Mountains of Russia in 1839. Perovskite materials were not, however, extensively studied for their electronic properties until the 20th century.

Perovskite materials experienced a rise in interest in their electronic properties in the 1960s as a result of the discovery that they possess superconducting characteristics at low temperatures. Researchers started looking into the photovoltaic characteristics of perovskite materials in the 1980s and 1990s, which led to the creation of perovskite solar cells (PSCs) in the 2000s.

Perovskite materials are currently one of the groups of materials that have received the most research attention in the fields of materials science and condensed matter physics. They are used in many different industries, such as energy, technology, and catalysis.

In addition to PSCs, a wide range of other photovoltaic and optoelectronic uses, including light-emitting diodes (LEDs), photodetectors, and lasers, have been investigated for perovskite materials. Additionally, their catalytic qualities have been investigated, especially in the context of water splitting for hydrogen synthesis [39] [40].

The study of perovskite materials is still expanding and changing, with new advancements and findings being made frequently. Perovskite materials are a promising area of research with potential for a broad variety of applications, despite the fact that there are still issues to be solved [39]. New research is required to further develop and optimize the stability, scalability, and environmental impact of perovskite materials, in order to unlock their full potential for use in various industries.

The structure of perovskite solar cells is typically composed of several sandwiched layers of materials. The substrate, the bottom layer, is frequently made of glass or a flexible substance like plastic. Transparent conducting oxide (TCO), which serves as a front conductor and lets light through to the perovskite layer, is layered on top of the substrate.

The TCO layer is followed by the perovskite layer, which acts as the light filter. Two charge transport layers, which are typically made of organic or inorganic materials, are normally sandwiched between the perovskite layer. Electrons and holes can travel more easily to the electrodes on either side of the device thanks to the charge transport layers. The back electrode is then created by depositing a metal electrode on top of the charge transfer layer.

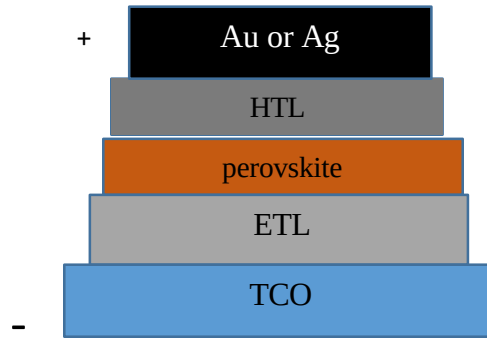


FIGURE 6: Planar Perovskite solar cell structure

2.6.1 TCO Layer (Transparent Conducting Oxide)

Light can reach the perovskite layer through the TCO layer, which serves as the front anode. Additionally, it offers a low-resistance pathway for electrons to leave the cell.

2.6.2 Perovskite Layer

By collecting photons and producing electron-hole pairs, the perovskite layer acts as a light absorber. Additionally, it offers charge transporters a low-resistance pathway through the cell.

2.6.3 Charge transport layer

These layers make it easier for electrons and holes to travel to the conductors on either side of the device. Between the perovskite layer and the back electrode is usually where the electron transport layer (ETL) is located, and between the perovskite layer and the TCO layer is where the hole transport layer (HTL) is located.

2.6.4 Regular and Inverted planar setup

FIGURE 7 shows the normal and inverted structure of the perovskite solar cells. In both of these structures the perovskite layer is sandwiched between ETL and HTL layers. The

HTL typically made of an organic substance like Spiro-OMeTAD, while the ETL is typically made of an electron-accepting material like TiO_2 . The layer arrangement is flipped in inverted PSC structures. The ETL is typically made of an organic substance, such as PCBM, and the HTL is typically made of an inorganic substance, such as NiO or PEDOT: PSS.

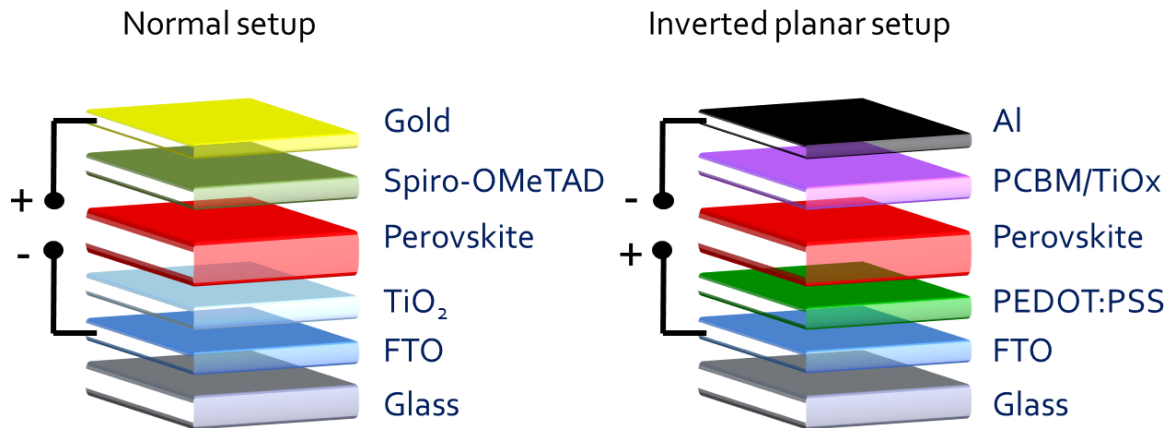


FIGURE 7: Normal and Inverted perovskite solar cell structure: source; www.zsw-bw.de/en/research/photovoltaics/topics/perovskite-solar-cells.html

The inverted structure's primary benefit is increased stability because it lessens the contact between the perovskite layer and the metal electrode, which can eventually cause degradation [41]. Due to less recombination at the interface between the HTL and the perovskite, inverted structures also have greater V_{oc} . In contrast to conventional structures, they typically exhibit greater series resistance and lower efficiency. The particular application and performance requirements dictate which PSC structure should be used. While inverted structures offer better stability they may trade off some efficiency, regular structures are frequently used and have attained high efficiencies [39] [42].

Recent advancements in the field of perovskite solar cells have focused on improving the stability and toxicity issues associated with the use of lead-based perovskites [49]. One approach is to develop novel perovskite substances that are less toxic and more stable, such as mixed-cation perovskites and tin-based perovskites. These materials have shown great efficacy and stability in PSCs and have the potential for use in other applications as well [43].

Another area of development is the design and optimization of perovskite solar cell architectures. Tandem cells and perovskite-silicon hybrid cells are two novel device designs that have been investigated by researchers in an effort to increase the productivity and stability of PSCs. To increase the scalability and reproducibility of these devices, researchers have also worked to optimize the fabrication methods for PSCs, including solution processing and vacuum deposition [44].

Other than photovoltaics, perovskite materials have also been researched for a number of other applications. Perovskite-based LEDs, for example, have demonstrated high efficacy and color purity, making them promising for display applications. Perovskite materials have also been investigated for their promise as thermoelectric materials and for their catalytic capabilities in the fields of fuel cells and water splitting [40].

CHAPTER 3

METHODOLOGY

3.1 Deposition methods

Deposition techniques fall into two broad categories high-cost techniques and low-cost techniques. *Sol-gel*, *spin coating*, *spray pyrolysis*, and *electrodeposition* are examples of low-cost methods, whereas pulsed laser deposition, molecular beam epitaxy and metal organic chemical vapour deposition are examples of high-cost methods. For researchers who are new to the field or who have limited resources, low-cost techniques are frequently more accessible and simpler to set up than high-cost ones. This makes them a good place to start. However, it's possible that less expensive techniques don't always result in products that are as good or as precisely controlled as those made using more expensive techniques.

On the other hand, expensive techniques provide fine control over the film's characteristics, including thickness, crystal structure, and makeup. They can also create heterostructures and multilayers, which are more complicated structures. These techniques are not better suited for research and development objectives because they are pricey and call for specialised tools and knowledge. Also, the prices of any ensuing product will also be high hence unreachable by many. [45] [46].

Generally, the method of choice relies on the particular needs of the application and the resources at hand. Low-cost methods might be preferred if cost is a major consideration, but high-cost methods might be needed if precise control over the film properties is essential. Therefore, for researchers who are new to the field, exploring novel applications or concepts, or working with limited resources, starting with inexpensive methods for depositing ZnO thin films can be an effective approach. Prior to moving on to more difficult and expensive techniques, it enables them to acquire useful experience and investigate the fundamental characteristics of ZnO thin films. In addition, when it comes to control of composition, low cost methods have proved more effective than their high cost counterparts.

In this study, we concentrated on strategies for depositing ZnO thin films at cheap costs. Due to their ease of use, affordability, and adaptability in creating thin films with precise properties, we specifically selected spray pyrolysis and spin coating methods. With the aid of these

techniques, we were able to fabricate and examine the fundamental characteristics of modified ZnO thin films, as well as the possible use for them as ETLs for perovskite solar cells.

3.1.1 Low-Cost ZnO Thin Film Deposition Techniques

The versatile substance zinc oxide (ZnO) has many uses in optoelectronics, sensors, and catalysis. A crucial stage in the creation of these devices is the deposition of ZnO thin films. ZnO thin sheets can be deposited using a number of low-cost techniques, each of which has benefits and drawbacks. The three most popular low-cost techniques for depositing ZnO thin films—Chemical Bath Deposition (CBD), Spray Pyrolysis Deposition (SPD), and Sol-Gel method are outlined below.

3.1.1.1 Chemical Bath Deposition (CBD)

ZnO thin layers can be deposited using the straightforward and inexpensive chemical bath deposition (CBD) technique. It entails an aqueous solution reaction between zinc ions and an appropriate reducing agent. ZnO nuclei are created when the zinc ions are reduced by the reducing agent, and they develop into thin films on the substrate. Glass, silicon, and plastic are just a few of the many surfaces on which CBD can create ZnO thin films. A schematic diagram of the CBD process experimental set-up is shown in FIGURE 8.

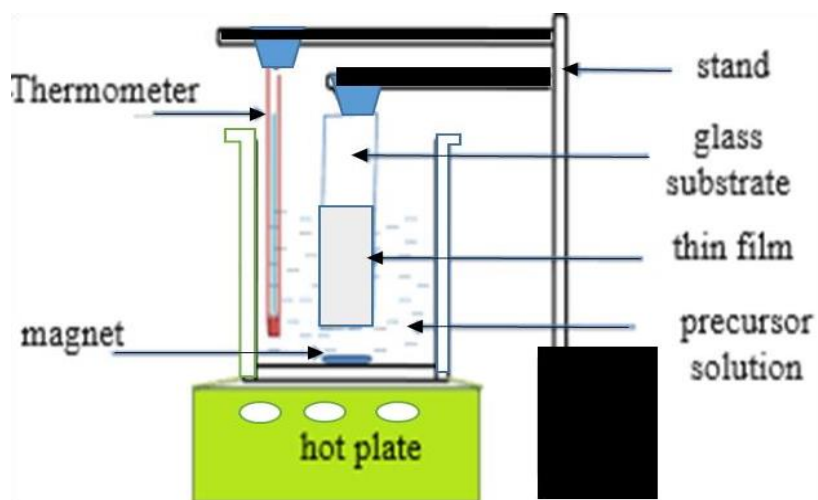


FIGURE 8: A schematic diagram showing the CBD experimental set-up

The ease of use and low expense of CBD are two benefits. It is appropriate for low-budget uses because it doesn't need high temperatures or specialized equipment. In contrast to expensive

methods, CBD-produced thin films might be of lower quality and have less influence over the film's characteristics. Numerous variables, including the pH, temperature, and precursor concentration of the solution, affect the film thickness, crystal structure, and optical characteristics of the films. Many researchers have looked into using CBD to deposit ZnO thin films. For instance, R. L. Swamy and S. S. Kumar et al [47], described using CBD to create ZnO thin films on a glass substrate. By changing the reaction time and temperature, the thickness and shape of the film were under control. The impact of various precursor concentrations on the optical and structural characteristics of ZnO thin films produced by CBD deposition on a silicon substrate was also studied in [48].

3.1.1.2 Spray Pyrolysis Deposition (SPD)

Another inexpensive technique for depositing ZnO thin sheets is called spray pyrolysis deposition (SPD). It entails the application of thin coatings by misting a precursor material solution onto a heated substrate. The heat breaks down the precursor solution, and the resulting ZnO distributes onto the substrate. ZnO thin films can be produced by SPD in a consistent, high-quality manner with excellent substrate adhesion. FIGURE 9 shows a picture setup of spray pyrolysis used in this project.

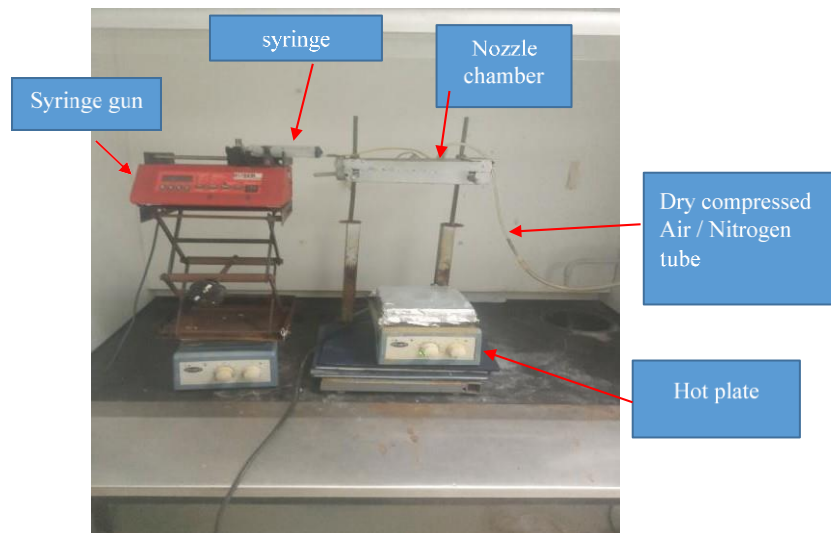


FIGURE 9: A photograph of spray pyrolysis setup

SPD has several benefits, including flexibility and affordability. It can be carried out with basic tools and readily scaled up to create large-area thin films. However, compared to expensive techniques, the control over the film's properties is minimal. The precursor concentration, substrate temperature, and spray parameters are just a few examples of the variables that have an impact on the layer thickness and morphology.

Among those who have reported on the impact of SPD on ZnO thin films, P. B. Patil et al [49] has reported that by changing the spray factors, such as the spray distance and solution concentration, the film thickness and morphology were managed. Y. Zhang, L. Hu, and Q. Zhang et al also reported on the impact of substrate temperature on the structural and optical characteristics of thin ZnO films formed through SPD deposition [48].

3.1.1.3 Sol-Gel Technique

A wet-chemical technique for depositing ZnO thin layers is the Sol-Gel Method. Metal alkoxides are hydrolyzed and condensed to create a sol that can be used to cast thin films. After applying the sol to the base, the solvent evaporates to create a gel, which is then heated to create the final thin ZnO layer. ZnO thin films of uniform thickness, high quality, and with excellent control over the film's properties, including porosity and crystal structure, can be made using the sol-gel method.

The flexibility and affordability of the Sol-Gel Method are two benefits. It can be carried out with basic tools and produces ZnO thin layers on a variety of substrates, including glass, silicon, and plastic. The film-growth process, however, is laborious and may involve several stages, which extends the processing period [50] [51] [52].

3.1.2 High-Cost Techniques for ZnO Thin Film Deposition

3.1.2.1 Pulsed Laser Deposition (PLD)

A well-liked, pricey technique for depositing ZnO thin layers is pulsed laser deposition (PLD). It involves the application of a plume created by the ablation of a target substance to a substrate using a laser. The deposition rate and layer characteristics can be precisely controlled due to the pulsed nature of the laser. With precise control over the film's properties, including

thickness, crystal structure, and orientation, PLD can create ZnO thin films of the highest quality.

PLD has the ability to create high-quality films with excellent control over the film's properties, which is one of its benefits. PLD is also appropriate for the development of heterostructures and complex multilayer structures. However, compared to inexpensive methods, PLD has significant equipment and operating expenses.

For the purpose of depositing ZnO thin films, PLD has been examined in a number of experiments. Researchers have reported using PLD to synthesise ZnO thin layers on a silicon substrate. Variations in the deposition parameters, such as the laser fluency and target-substrate distance, were used to regulate the film properties, including the surface morphology and optical characteristics. The optical and electrical characteristics of ZnO thin films deposited using PLD on silicon substrates were investigated. It was discovered that the deposition variables, such as the laser fluency and substrate temperature, had an impact on the film characteristics [53] [54] [55].

3.1.2.2 Molecular Beam Epitaxy (MBE)

Another expensive technique for depositing ZnO thin layers is Molecular Beam Epitaxy (MBE). In a vacuum chamber, material is deposited onto a substrate using a stream of evaporating material. With precise control over the film's properties, including thickness, composition, and crystal structure, MBE is able to create ZnO thin films of the highest quality.

The capacity of MBE to create high-quality films with excellent control over the film properties is one of its benefits. MBE is also appropriate for the growth of heterostructures and complicated multilayer structures. However, compared to low-cost methods, MBE has expensive equipment and operating expenses.

For the purpose of depositing ZnO thin films, MBE has been examined in a number of experiments. N. Wang et al reported using MBE to create ZnO thin films on a sapphire substrate. Variations in the deposition parameters, such as the substrate temperature, annealing temperature, variation of thickness and the Zn/O flux ratio, were used to regulate the film properties, including the crystal structure and optical properties. The influence of substrate orientation on the structural and electrical characteristics of GaAs_{1-x}Bi_x thin films formed by MBE deposition was discussed by S. Alhassan, D. de Souza, A. Alhassni et al [56] [57] [58].

3.1.2.3 Metal Organic Chemical Vapor Deposition (MOCVD)

Another well-liked, pricey technique for depositing ZnO thin layers is Metal Organic Chemical Vapor Deposition (MOCVD). In order to create a solid thin layer on a substrate, metal organic precursors must first decompose in a gas phase. With exact control over the film's properties, including thickness, crystal structure, and composition, MOCVD can create ZnO thin films of the highest quality.

The capacity to create high-quality films with excellent control over the film properties is one of the benefits of MOCVD. Complex multilayer frameworks and heterostructures can be grown using MOCVD. However, compared to low-cost methods, MOCVD has expensive equipment and operating expenses [59] [60].

Atomic layer deposition (ALD), radio-frequency magnetron sputtering (RFMS), and electron beam evaporation (EBE) are other expensive techniques for depositing ZnO thin layers. ALD can create high-quality ZnO thin films with exact control over the film's properties, including thickness and composition [61]. It has been reported that RFMS is appropriate for depositing ZnO thin films with good optical and electrical properties due to its ability to precisely control film thickness. The properties of the resulting thin films can be impacted by the deposition parameters, such as substrate temperature and RF power, as described in [62].

3.2 Deposition of the perovskite layer

A common method for depositing thin sheets, such as the perovskite layers found in perovskite solar cells, is spin coating. The perovskite layer, which absorbs light and produces electrons and holes that are then gathered by the electron transport layer (ETL) and hole transport layer (HTL), respectively, is an essential part of the PSC. As shown in FIGURE 10 a spin coating is the process of coating a substrate with a perovskite precursor solution before rapidly spinning the substrate to create a uniformly thin film.

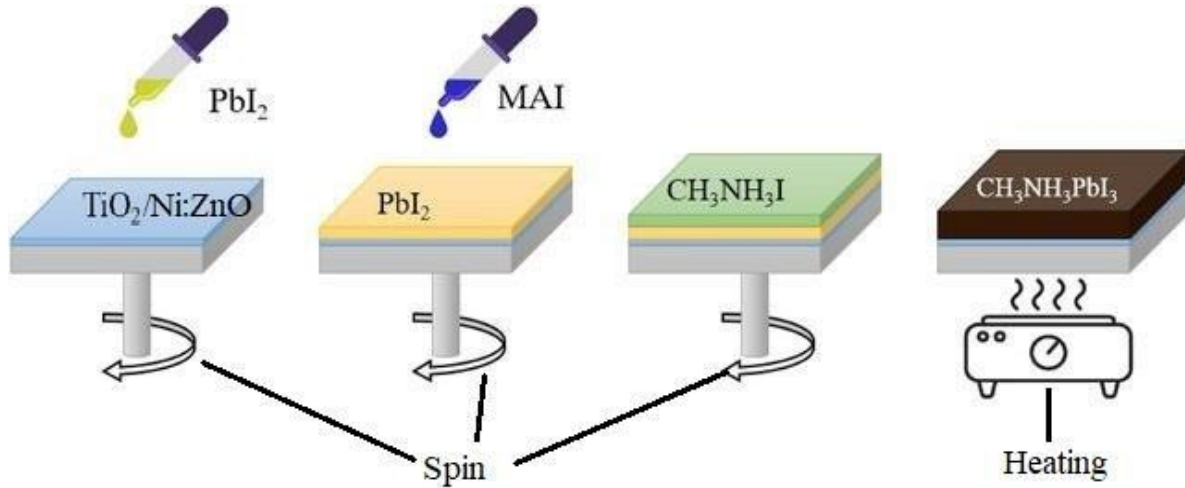


FIGURE 10: A diagram of Spin coating process [63]

Lead iodide (PbI_2), methyl ammonium iodide (MAI), and a fluid, such as dimethylformamide (DMF) or dimethyl sulfoxide, are the usual components of the perovskite precursor solution. Due to centrifugal force, the rotating procedure causes the precursor solution to disperse and create a uniform film.

Spin speed, spin duration, precursor solution concentration, and composition all have a significant impact on the perovskite layer's quality when it is formed by spin coating. The film's thickness and uniformity are determined by the spin speed, whereas the perovskite layer's crystallinity and morphology are influenced by the spin duration. The crystallinity, morphology, and optical characteristics of the perovskite layer can all be impacted by the concentration and makeup of the precursor solution.

The ease and adaptability of spin coating is one of its benefits. Spin coating is an easy-to-use method that only needs the most basic tools and knowledge. The procedure is suitable for a variety of PSC applications because it is readily optimized for various perovskite materials and device configurations. Additionally, spin coating can create perovskite layers with high efficiency and stability that are extremely uniform and reproducible [64] [65] [66] [63].

Spin coating has some drawbacks despite its benefits. Controlling the morphology and crystal structure of the perovskite layer, which can impact the PSC's performance and stability, is one of the major challenges in spin coating. The perovskite layer may crack or develop other flaws as a result of the spinning process' high spin speed and shear pressures, which could lower the

device's efficiency and stability. The use of hazardous and moisture-sensitive chemicals in the perovskite precursor solution can also raise issues with safety and the environment [67].

3.3 HTL/ Conductive /layer deposition

In a quest for cheaper, stable and easily processable materials in the manufacturing solar cells, Carbon based designs have taken the center stage. The use of Carbon allows for the removal of expensive materials such as Gold (Au) and silver (Ag) as counter electrodes and the commonly used HTLs such as spiro-Ometad and Poly(3,4-ethylenedioxythiophene) poly (styrene sulfonate) (PEDOT:PSS). However this substitution leads to compromised photo electric performance as to date the highest achieved efficiency of HTM free solar cell is 12.8% [68] [69] solar cell efficiencies. Carbon layers could be deposited through various methods such as screen printing and doctor blade method. [70]. FIGURE 11 shows a diagram of Dr blade deposition method which is the employed method in this research.

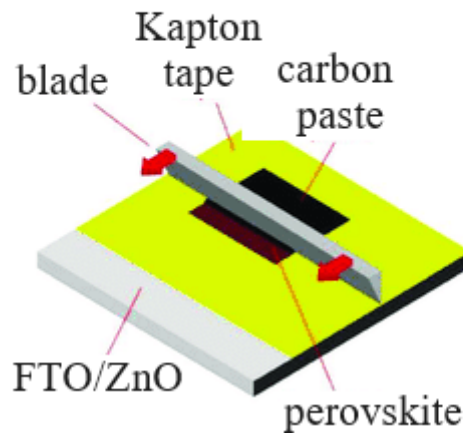


FIGURE 11: A schematic diagram of doctor blade method [71]

Carbon paste is deposited onto a substrate using the doctor blade deposition method as shown in FIGURE 11. Using a blade to spread a thin layer of carbon paste onto a substrate guarantees

that the paste is distributed uniformly throughout the substrate. In comparison to other deposition methods, doctor blade deposition has a number of benefits, including scalability, uniformity, thickness control, cost effectiveness, and reproducibility [71] [72]

3.4 EXPERIMENTAL PROCEDURE

3.4.1 Synthesis of Ni-ZnO seed layer

To enable the growth of nano-rods structures, a seed layer was first grown on glass slides of measurement 7.4 cm x 2.2 cm using the spray pyrolysis method as shown in FIGURE 9. Glass slides were first soaked for 1 hour in acetone, then placed in a solution of ethanol and deionized water for 20 min in an ultrasonic bath. Afterwards they were dried in compressed air and were stored in an airtight container for later use [73]

Zinc Acetate dehydrate ($\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$) (Alfa Aesar, Kandel, GERMANY, purity 97+ %) salt was dissolved in ethanol to prepare a 0.05 M concentration solution under constant steering for 1 h. 0.05M ethanolamine was then added to the precursor solution as a stabilizing agent. Nickel (II) Nitrate hexahydrate ($\text{N}_2\text{NiO}_6 \cdot 6\text{H}_2\text{O}$) was used to dope ZnO ($\text{Ni}_x\text{-ZnO}$) for $x = 0, 2, 4, 6$ and 8 %. 20 ml of the precursor solution was loaded in the syringe and deposited at a rate of 2 ml/min at deposition temperature of 350 °C with a nozzle to glass slide height of 25 cm under nitrogen gas atmosphere. Before deposition glass slides were preheated for 10 min and after deposition substrates were annealed in air at 350 °C for 20 min [74].

3.4.2 Synthesis of Ni-ZnO nano rods

Ni-ZnO nanorods were prepared by chemical bath deposition method. The setup was prepared as in FIGURE 8. A 0.05M precursor solution with varying dopant (Ni) concentrations of (0, 2, 4, 6 and 8 %) was prepared using Zinc Chloride salt (Sigma-Aldrich, USA, purity 99.99%) and Nickel (II) Nitrate hexahydrate (Sigma-Aldrich, USA, 99.999%). For every 85 ml bath, 8.5 ml of 0.03 M Hexamethylenetetramine (HTMA) (Sigma-Aldrich, Germany 99%) surfactant was added under constant stirring. The surfactant is known to help facilitate the growth of nano-rods inhibiting the growth on the axial plane [75]. Then ammonia solution was added drop by drop until a clear solution was obtained. All mixing and stirring were done under normal room temperature (25 °C). Respective seed layered glass substrates were then suspended vertically upwards inside a 100 ml beaker each and the prepared solutions were poured in the

beakers. The bath temperature was maintained at 95 °C for 2 hrs. After 2hrs the substrates were removed and rinsed in running deionised water to remove residuals and were left to cool at room temperature overnight. Finally, the substrates were annealed at 350 °C for 1 hr under normal atmosphere then cooled and stored in an airtight container for further analysis.

3.4.3 Deposition of MgO layer

A thin layer of MgO was deposited on top of the Ni-ZnO nanorods using spray pyrolysis method following a set up as in FIGURE 9. A 0.1M of solution was prepared by dissolving 1.84 g of MgCl_2 in 200 ml of deionised water. 20 ml of EA was added to the solution and the mixture was stirred for 20 min at normal room temperature. Then 10 ml of the mixed solution was deposited at a rate of 0.5 ml/min with a nozzle to substrate height of 25 cm and the deposition temperature was set at 350 °C. Then finally the MgO-EA layer was annealed at 350 °C for 1 hour. [76] [77].

3.4.4 Preparation and deposition of dyes

0.005M of Rose Bengal (RB) dye and Brilliant Black BN (BBBN) dye were separately prepared. Two beakers were filled with 20 ml of ethanol. 0.087 g of BBBN was added to the first beaker and 0.101 g of Rose Bengal was added to the second beaker. Both solutions were stirred for 20 min at room temperature. Afterwards the two beakers were covered with aluminium foil to prevent light absorption as light is known to activate dye and cause degradation when a dye solution is not under use. Then 1 ml, each of, RB and BBBN was administered drop wise on top of the MgO-EA to obtain MgO-EA/RB and MgO-EA/BBBN layers respectively. Samples were then covered with aluminum foil and left to dry overnight and kept covered until further use [78].

3.4.5 Deposition of the perovskite layer/carbon layer

In order not to temper with the dyed active layer a method of electron beam deposition technique was deployed to deposit lead iodide layer using HHV TF500 machine shown in FIGURE 12.



FIGURE 12: A photograph of HHV TF500 machine

Firstly, 0.8 grams of lead iodide was scooped into a graphite crucible and placed into the deposition chamber. During the deposition the vacuum chamber was kept at 4.62×10^{-5} mbar while current was increased from 5 mA to 45 mA by steps of 1 mA every 10 seconds until all the powder have been evaporated. This formed a thin and neat PbI_2 film. [79]

Then a 0.5M solution of MAI was prepared by mixing 0.476 g of MAI with 30 ml of iso-propanol at room temperature stirring until a goldish-brown uniform colour was obtained indicating that the MAI has fully dissolved. Then using a syringe and for all samples, two drops of the solution were dropped on the PbI_2 layer until the surface was fully cover. The MAI solution was left to soak for 10 min on the PbI_2 after which all samples were dried using a WS- 650HZB-23NPPB/UD30 spin coater. The drying conditions were set at 1500 rpm for 10 sec. After drying was complete the samples were annealed at 120°C for 15 min. During this process a colour change from yellowish to dark brown was observed as shown in FIGURE 13 [97].

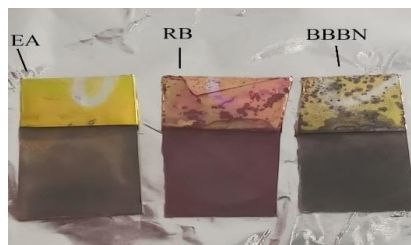


FIGURE 13: A photograph showing samples after the deposition of the perovskite layer for MgO-EA, MgO-EA/RB and MgO-EA/BBBN

A final layer of the carbon paste was deposited using the doctor blade method as shown in FIGURE 11. The final samples can be seen in FIGURE 14.

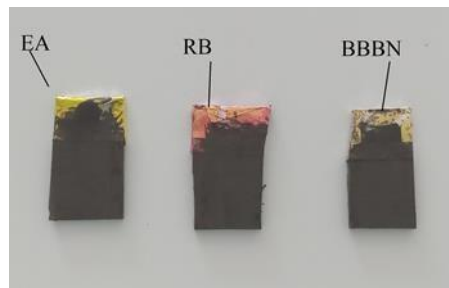


FIGURE 14: A photograph showing solar samples after the deposition of carbon paste.

Lastly a thin layer of carbon paste was doctor bladed on an FTO coated glass and it was used as positive contact anode by pressing against the deposited carbon during testing of solar cells.

3.4.6 Characterization of thin films

Structural properties were analysed using XRD (Bruker 8 Advanced) machine radiating $\text{CuK}_{\alpha 1}$ of $\lambda_{\alpha 1} = 1.5060 \text{ nm}$. The XRD measurements were obtained within a 2θ range of 10° to 80° . Optical analysis was performed using the UV/Vis/NIR (Perkin Elmer Lambda 750) spectrophotometer from 250 nm to 1100 nm whereas vibrational modes were characterised using the Raman spectrophotometer (Labram HR Evolution Raman Spectrometer equipped with a laser excitation wavelength of 532 nm). Electrical properties were obtained using the (Ecopia AMP 55T HMS-5300-HMS-5500) Hall effect system. High-resolution field emission scanning electron microscopy (FESEM, Carl Zeiss AG) with acceleration voltage of 2 kV was used to study the surface morphology of thin films. The I-V characteristics of the solar cells were determined by the variable resistor method as shown in FIGURE 15. In this method, a solar cell was placed under illumination while the resistance (R) was varied from minimum to maximum. Then the corresponding voltage and current were recorded. The short circuit current (I_{sc}) was obtained when R was set at 0Ω and the open circuit voltage (V_{oc}) was obtained when the R was maximum.

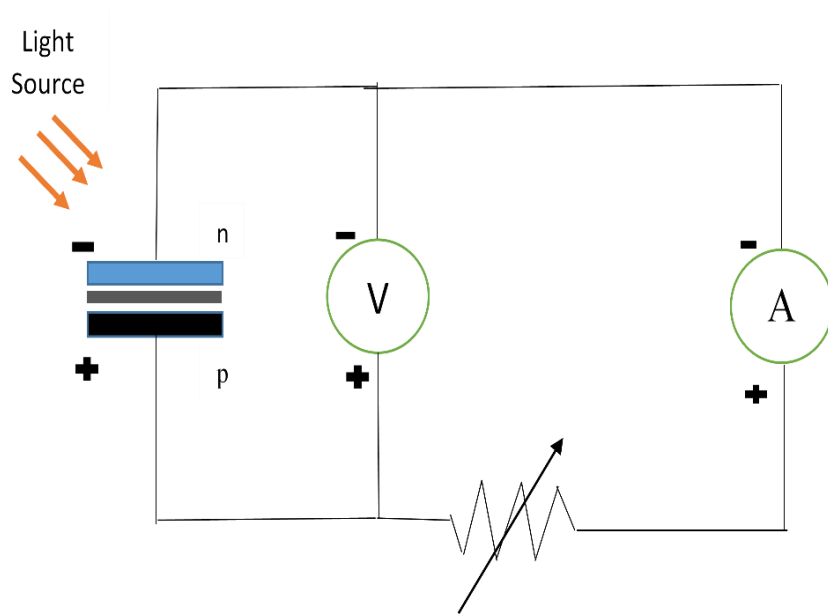


FIGURE 15: A circuit diagram used in solar cell testing

CHAPTER 4

RESULTS AND ANALYSIS

4.1 ANALYSIS OF Ni-ZnO THINFILMS

4.1.1 STRUCTURAL PROPERTIES

4.1.1.1 XRD analysis

FIGURE 16 shows XRD patterns of undoped and Ni-doped ZnO. A strong and preferred orientation favouring a hexagonal wurtzite structure with a presence of Zinc-blende was observed across all samples as indicated by doublet peaks shown on the zoomed portion of the most dominant (002) peak shown in FIGURE 16 (b). This doublet behaviour can be attributed to similarities in anionic coordination of the phases [80]. The dominant (002) peak reveals a thermodynamically preferred and favoured growth along the c-axis as well as high crystallinity of the samples as indicated by the sharpness of the peak [74]. The absence of (111) peak of NiO indicates that there was no formation of any secondary oxides or unsubstituted residual NiO.

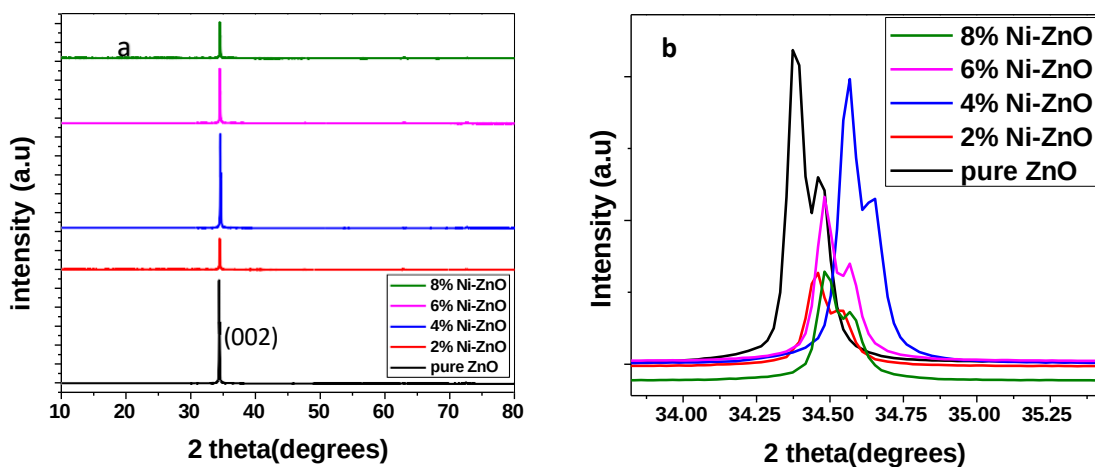


FIGURE 16: XRD patterns for $Ni_x - ZnO$ where $x = (0, 2, 4, 6, 8 \%)$, (a) showing the intensity from 2θ 10-80 and (b) zoomed portion of the (002) peaks.

To further understand the impact of Ni dopant on the structure of ZnO, the interplanar spacings (d) were calculated using equation 1 [81].

$$n\lambda = 2d\sin(\theta) \text{ -----}6$$

where θ is the Bragg's angle, λ is the wavelength and $n = 1$. The obtained d values are recorded in Table 1. The average crystallite sizes (D) of were calculated using the Scherrer relation given as:

$$D = \frac{k\lambda}{\beta\cos\theta} \text{ -----}7$$

where k is 0.94 and β is the full width at half maximum (FWHM). A reduction in the interplanar spacing values and crystallite sizes upon the introduction of nickel dopant was observed. This decrease can be associated with the observed peak shifting towards higher Bragg's angle as shown in FIGURE 16(b), with 4% concentration being shifted the most and having the lowest d value. The decrease in the crystallite sizes might be due to the apparent reduction of the surface tension upon nucleation caused by distortion of the host lattice at the introduction of impurities [74]. The lattice parameters were calculated using equation 8 [81] [82] and the obtained values of d , D and the lattice parameters a and c are recorded in Table 1.

$$\frac{1}{d} = \frac{4}{3} \left[\frac{h^2+hk+k^2}{a^2} \right] + \frac{l^2}{c^2} \text{ -----}8$$

The observed decrease in the lattice parameters value is attributed to the linear mismatch of the ionic radii of Ni^{2+} (radii of 0.55 Å) and Zn^{2+} (radii 0.60 Å) which occurs during doping [83] [84].

Table 1: Calculated structural specifications for the prepared undoped ZnO and $\text{Ni}_x\text{-ZnO}$ thin films

Ni %	d-spacing (Å) (002)	Crystallite size(nm)	c (Å)	a (Å)	c/a	L (Å)
0	2.6044	75.8	5.2104	3.2416	1.6074	1.9748
2	2.6027	56.6	5.2002	3.2546	1.5978	1.9790
4	2.5914	72.9	5.1926	3.2461	1.5996	1.9746
6	2.5971	67.0	5.1999	3.2469	1.6015	1.9758
8	2.5965	70.6	5.1993	3.2462	1.6017	1.9754

The bond length (L) of Zn-O was calculated using equation,

$$L = \sqrt{\left(\frac{a^2}{3}\right) + (0.5 - u)^2 * c^2} \dots\dots\dots 9$$

where $u = \left(\frac{a^2}{3c^2} + 0.25\right)$ is the parameter that accounts for the numeric separation between atoms with respect to the c-axis [85]. The obtained values are within the range (1.9746 - 1.9790 Å). A longer bond length of 1.9790 Å was observed at 2% Ni doping and this could be correlated to the small c/a ratio which was observed. It was observed that the smaller the c/a ratio the longer the bond length hence less strain along the c-axis [86] [87]

4.1.1.2 RAMAN analysis

The Raman spectra for Ni_x – ZnO is shown in FIGURE 17. Intensity peaks were observed at 251 cm⁻¹, 441 cm⁻¹ and 558 cm⁻¹ respectively. A red shift was observed at 251 cm⁻¹ peak indicating an E₂ low asymmetric tail which is normally associated with ZnO lattice stress, reduction in crystallite/particle size and scattering energy losses due to doping [88] [89] [90]. The 441 cm⁻¹ peak is generally assigned to the Zn-O bond indicating an E_{2H} vibrational mode. The hexagonal wurtzite structure was well preserved as represented by intense peaks at 441 cm⁻¹. The 558 cm⁻¹ peak is attributed to A₁ Longitudinal optical component of the active Raman modes. This mode has previously been associated with the presence of impurities or a defective lattice [91]. The A₁ LO mode is noted to intensify as Ni dopant concentration increases. These results were found to be consistence with the XRD results indicating successful incorporation of Ni within the ZnO structure. Synthesis method, impurities and oxygen vacancies are known to influence the hexagonal structure leading to the appearance of vibrational modes near the Brillouin zone [74] [92] [93].

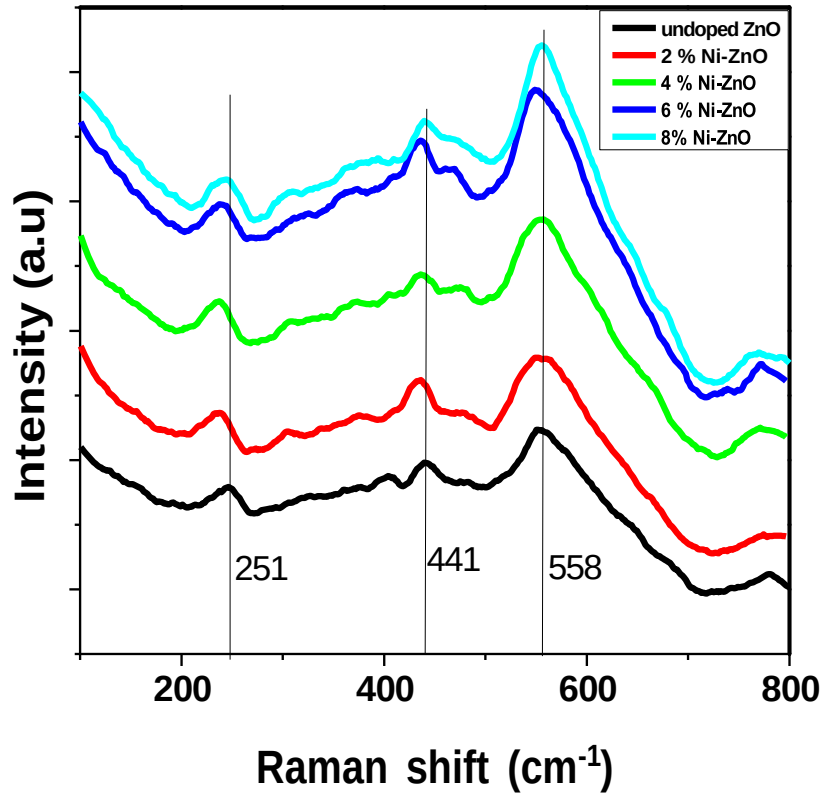


FIGURE 17: Raman spectra for $\text{Ni}_x - \text{ZnO}$ where $x = (0, 2, 4, 6, 8 \%)$

4.1.2 MORPHOLOGICAL analysis

FESEM and AFM techniques were employed to study the morphology of the films. The high and low magnifications of pure ZnO and Ni-doped ZnO are shown in FIGURE 18. Dense nanorods are observed before and after doping with nickel. Some differences are observed in the shape and size of the tips of the nanorods. Hexagonal-like and well dispersed nanorods are observed for the pure ZnO. However, upon doping with Ni, the ends become more spherical and a bit clustered. The presence and elemental composition of Ni in the ZnO films was investigated by employing the EDX technique. The spectrum in FIGURE 17 shows the EDX spectra of nickel doped ZnO which shows successful incorporation of Ni ions into the ZnO lattice structure.

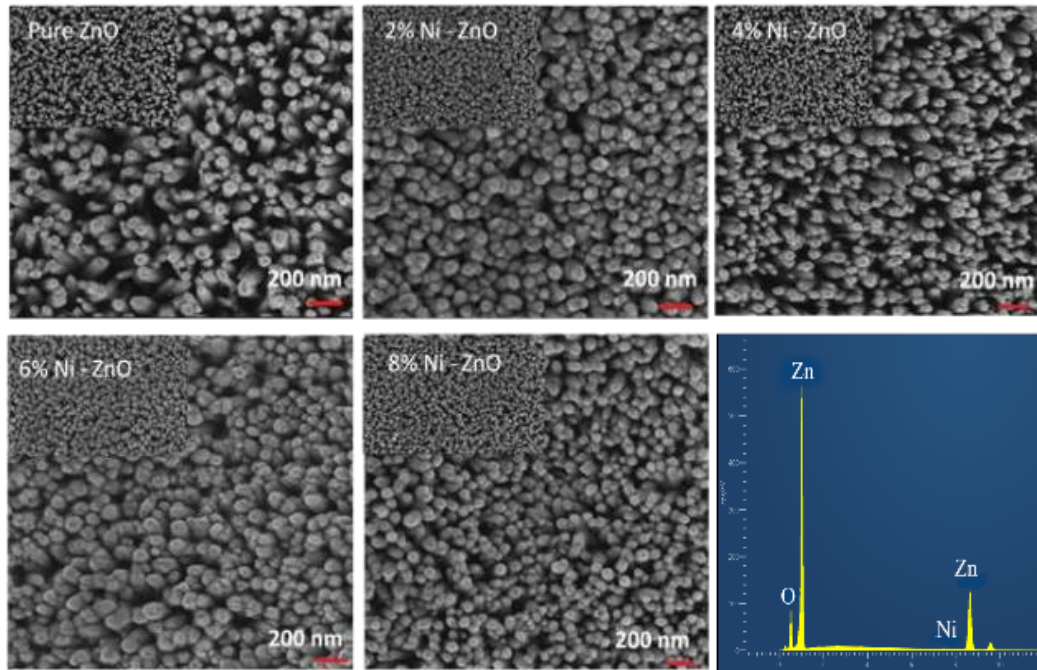


FIGURE 18: FESEM micrographs of pure ZnO and 2, 4, 6 and 8% Ni doped ZnO, EDX spectrum for $\text{Ni}_x - \text{ZnO}$

FIGURE 19 shows 3D AFM micrographs of the fabricated $\text{Ni}_x\text{-ZnO}$ thin films, which were analyzed to determine the grain size as well as the surface roughness of the samples.

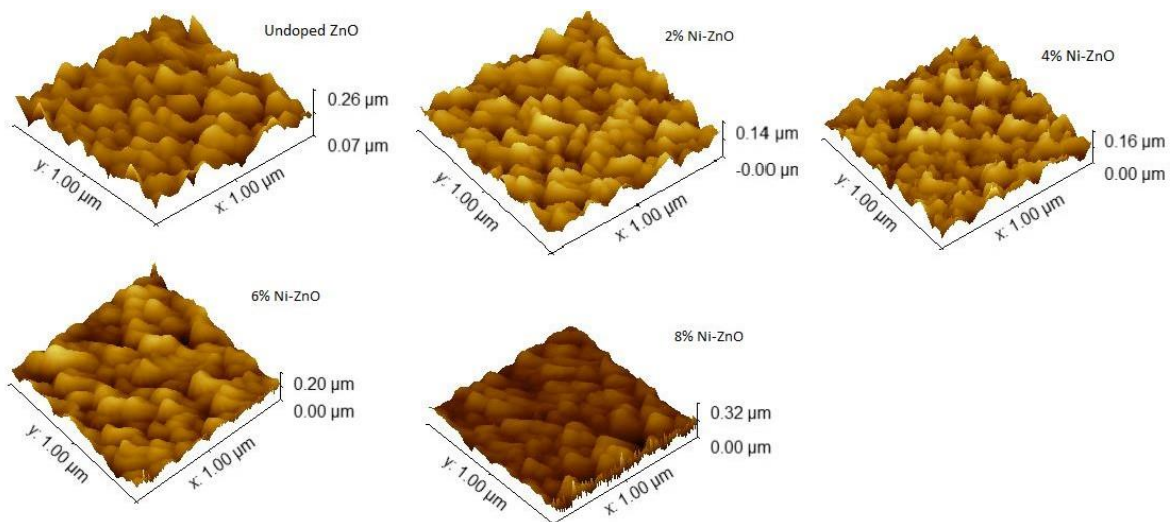


FIGURE 19: 3D AFM images showing surface morphology of the thin films

The estimated values of grain sizes and surface roughness are shown in Table 2. The introduction of Ni dopant resulted in an increment of the mean roughness making changes to the ZnO matrix which might be correlated to the successful in-cooperation of Ni ions into the ZnO lattice [94] [95].

Table 2: Surface morphological characteristics of Ni_x-ZnO X= (0, 2, 4, 6 and 8 %).

Ni %	Grain size radius (nm)	Average grain height (nm)	Surface Mean Roughness (nm)
0	48.3	150.0	16.3756
2	38.5	80.1	16.7288
4	31.5	84.0	16.7256
6	46.2	100.0	18.0545
8	45.2	122.0	18.7289

The grain size (radius and height) was observed to be within the range 31.5 nm - 48.3 nm and 122.0 nm - 150.0 nm respectively. It appears that the introduction of Ni ions led to the overall reduction in grain size with respect to the undoped ZnO. FIGURE 20(f) shows the average grain radius and the height distribution of the fabricated samples. It was observed that both average grain radius (48.3 nm) and height distribution (150 nm) is higher for the undoped Ni-ZnO and lower for doped samples. The general distribution was lower at 2% and 4% doping ratios, it then went up after the 4% at 6% and 8%. The smallest average grain size radius was observed to be 31.5 nm at 4% and the least average height was observed to be 80.1 nm at 2%. This inhibition of grain size growth is understood to occur due to the small ionic radii of Ni⁺² ions [83] [84]. This effect was also observed from the XRD analysis. The overall grain size distribution for each of the fabricated thin film is shown in FIGURE 20 (a)-(f).

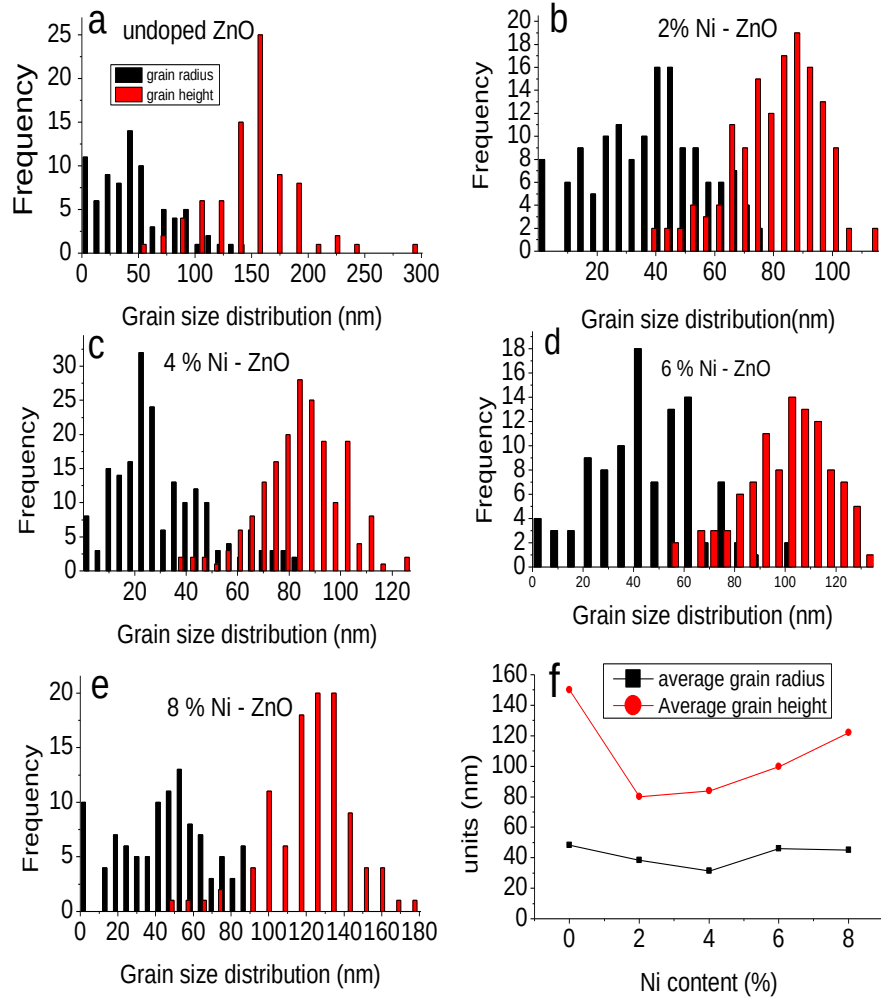


FIGURE 20: Histograms showing grain size distribution for pure ZnO and 2, 4, 6 and 8% Ni doped ZnO

4.1.3 OPTICAL PROPERTIES

FIGURE 21 shows the obtained optical transmittance and estimated energy band gap of the thin films. The transmittance spectra in FIGURE 21(a) shows that the 2% Ni doped ZnO sample exhibited higher optical transmittance in the visible region when compared to other samples. In general, an increase in dopant concentration appears to reduce optical transmittance. However, in some instances doping is known to optimize optical scattering due to reduced voids and homogenous uniform particle distribution which was observed at 2% Ni dopant [96]. The measured transmittance was utilized to determine the optical band gap energy of the samples through the use of the Tauc plot model. Firstly, the absorption coefficient (α) was estimated through equation 10.

$$\alpha = \frac{1}{t} \ln \frac{1}{T} \dots\dots\dots 10$$

with t and T being the equivalent film thickness and the transmittance values respectively. The evaluated absorption coefficient was then used in equation to calculate the band gap.

$$(\alpha h\nu) = A(h\nu - E_g)^n \dots\dots\dots 11$$

where A is a constant and n assumes $\frac{1}{2}$ for direct allowed transition usually associated with ZnO. A plot for $(\alpha h\nu)^2$ against $h\nu$ is shown in FIGURE 21(b). The tail band extrapolation towards the x- intercept and the $h\nu$ intercept is the estimated value of the band gap energy. The obtained values of the band gap energy are denoted as E_g Tauc, shown in Table 3.

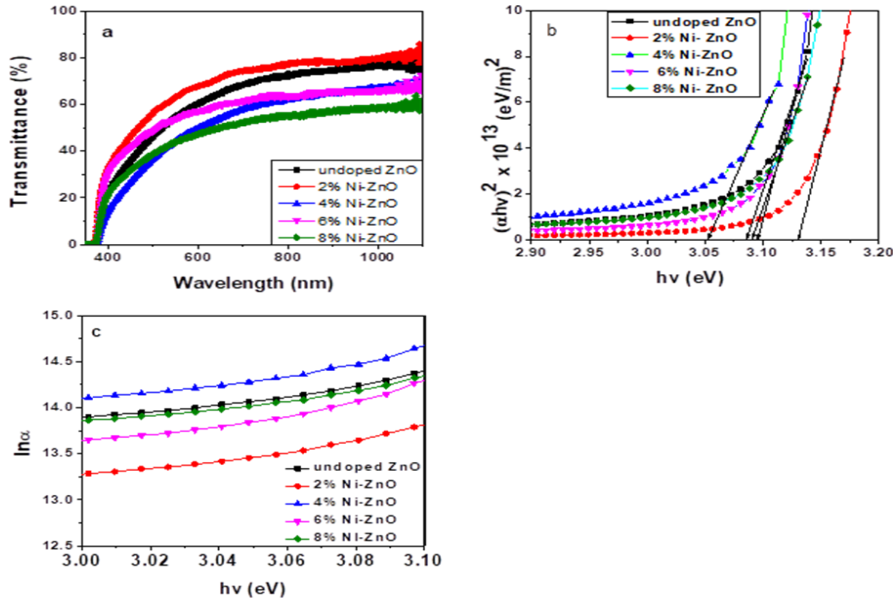


FIGURE 21:(a) Transmittance spectra of the prepared $\text{Ni}_x - \text{ZnO}$ $x = (0, 2, 4, 6 \text{ and } 8 \%)$. thin films. (b) Tauc plot of $(\alpha h\nu)^2$ against. (c) $\ln(\alpha)$ against $h\nu$ for the prepared $\text{Ni}_x - \text{ZnO}$ thin films. For the Urbach plots, plot a scatter and fit with the line of best fit.

The estimated values of the band energy were found to be increasing with dopant concentration and within the range of 3.07eV (undoped) to 3.21 eV (8% doped), making this material suitable for solar application as an electron transport layer. The variation of the band gap energy of pure and doped samples may be attributed to the disorder of the films. The increase in band gap energy could be explained using the Burstein-Moss effect which presuppose that increase in dopant concentration leads to increase in fermi level in the semiconductor conduction band, resulting from increased charge carriers and structural disorder [97] [98] [99]. To verify this assumption, Urbach energy was determined. The Urbach energy (E_u) is defined by the band tail energy, using equation, which shows the correlation between the absorption coefficient and the photon energy.

$$\alpha = \alpha_0 e^{\frac{h\nu}{E_u}} \dots\dots\dots 12$$

The logarithm of this equation gives,

$$\ln(\alpha) = \ln(\alpha_0) + \frac{h\nu}{E_u} \dots\dots\dots 12(a)$$

Table 3: Estimated bandgap energy and Urbach energy for Ni_x-ZnO

Ni %	E _{g(Tauc)} (eV)	E _U (meV)
0	3.07	85.1
2	3.12	81.9
4	3.13	85.4
6	3.16	68.3
8	3.21	93.5

A graphical relationship between of $\ln(\alpha)$ and the photon energy is shown in FIGURE 21(c) Urbach energy E_u can be determined by taking the inverse of the slope of equation 12(a) [100]. Higher values of Urbach energies at 4% and 8% doping concentrations can be attributed to increased structural disorders [101] Presence of these defects is evident from the absence of a sharp cut-off edge.

4.1.4 ELECTRICAL PROPERTIES

FIGURE 22 shows variation of electrical conductivity and resistivity with Ni dopant concentration. The obtained values of conductivity, resistivity, bulk concentration, mobility and figure of merit are recorded in Table 4.

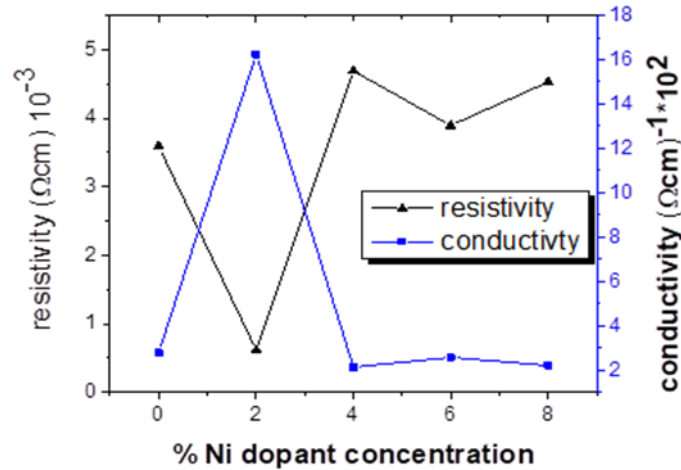


FIGURE 22: Variation of resistivity and conductivity for Ni_x-ZnO $x = (0, 2, 4, 6$ and $8 \%)$ thin films

Table 4: Measured electrical parameters for Ni_x-ZnO $x = (0, 2, 4, 6$ and $8 \%)$ thin films

Ni Molar Concentration %	Bulk concentration (/cm ³) x 10 ¹⁹	Sheet concentration (/cm ²) x 10 ¹⁶	Sheet resistance (Ω/□) x 10 ²	Resistivity (Ωcm) x 10 ⁻³	Conductivity (1/Ωcm) x 10 ²	Mobility (Cm ² / Vs)	Figure of merit(□/Ω) x 10 ⁻⁶
0	38.40	0.1034	13.35	3.590	2.780	0.647	1.681
2	07.62	0.0158	2.965	0.616	16.24	6.717	22.71
4	105.34	0.2939	16.80	4.688	2.133	1.984	0.162
6	62.29	0.1730	13.95	3.890	2.569	0.045	0.941
8	21.16	0.0590	16.23	4.530	2.207	2.261	0.147

The obtained electrical properties of Ni_x-ZnO thin films are tabulated in Table 4. The introduction of nickel as a dopant led to increased resistivity except at 2%. The 2% doped film

showed the lowest resistivity hence a corresponding higher conductivity and mobility value at this dopant level %. It appears that 2% Ni doping gives an optimum and uniform distribution of Ni ions within the ZnO lattice structure resulting in superior electrical properties. This behaviour is often explained by the impurity *d*-band splitting model and optimized oxygen vacancies leading to increased dipole moment. Low conductivity was observed at higher doping levels of 4-8%. Generally, oxygen vacancies are associated with high electrical conductivity. However, excess dopant ions are known to lead to the build-up of charge carrier traps which in turn reduces carrier mobility as oxygen vacancies are compensated by these excess ions [98] [102] [103] [104]. P-Y Chen et al [105] also reported that 2% Ni doping of ZnO lead to improved device PCE performances when compared to 1% doped and the undoped ZnO. It is generally understood that bigger grain size allows for easier transition of electrons leading to improved conductivity measurements. However, we observe that the 2% has improved conductivity despite it having smaller average grain size. This observation can be attributed to a shorter height leading to a thinner and more transparent thin film as was observed. This is advantageous as resistivity (ρ) is known to be proportional to thin film thickness as shown in equation 13.

$$\rho = R_s t \dots\dots\dots 13$$

where R_s is sheet resistance and t is the film thickness [106]. The doping of ZnO with Nickel enhances the overall magnetic properties and conductivity of ZnO structure [107]. The quality of the thin films can also be evaluated using the figure of merit (FOM) given by using equation 9

$$F = \frac{T^{10}}{R_s} \dots\dots\dots 14$$

Where T is the average transmittance in the visible spectrum range and R_s is sheet resistance [107]. The highest figure of merit of $22.71 \times 10^{-7} (\Omega/\square)^{-1}$ was obtained at 2% Ni doping as shown in Table 4. This is correlated to higher transmittance in the visible region around 550 nm and low sheet resistance. It can therefore be reasoned that the 2% Ni doped ZnO is highly likely to perform better as an ETL in solar cells.

4.2 ANALYSIS OF THE PROPERTIES OF THE PEROVSKITE SOLAR

4.2.1 STRUCTURAL ANALYSIS

4.2.1.1 XRD analysis

FIGURE 23 shows the XRD pattern for the fabricated FTO/Ni-ZnO/MgO-EA layers scanned from $2\theta = 10^\circ$ to 90° . From the profile it can be observed that the most dominant peak is the (002) ZnO peak which indicates a preserved hexagonal wurtzite structure [108] as observed by others [109] [110] [111]. FTO peaks were observed at 27.5° and 52.3° , while ZnO peaks were observed at 35.3° , 48.7° , 63.6° and 73.31° corresponding to (002), (101), (102), (103) and (004) plane and lastly the MgO peaks observed at 38.7° and 66.2° . and were

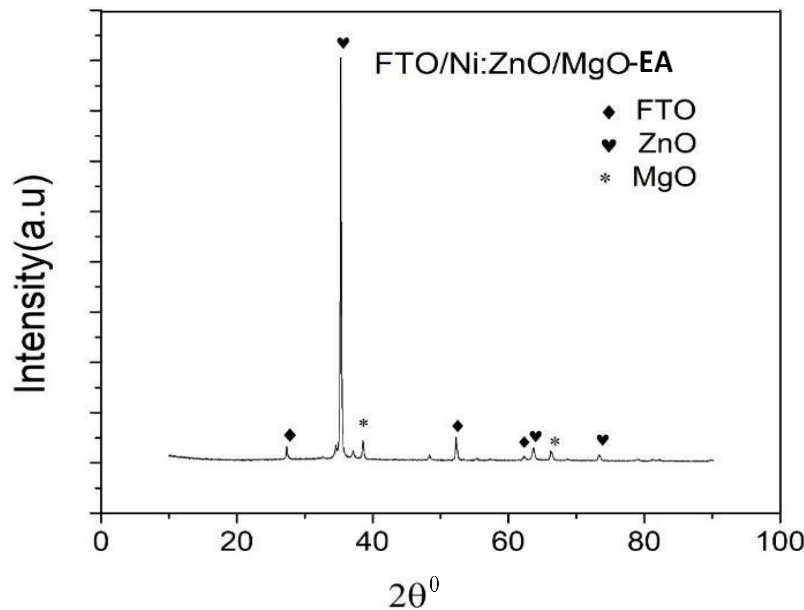


FIGURE 23: XRD pattern for FTO glass substrate coated with layers of Ni-ZnO and MgO-EA

matched to (111) and (222) planes, respectively. The presence of these various individual peaks that can be indexed to either ZnO or MgO indicates that this is not a single layer but rather a composite layer as intended and depicted by SEM micrographs in FIGURE 24 [112].

A thin coat of MgO can clearly be observed as shown in FIGURE 23 labels A and B over the Ni-ZnO nanorods as expected. According to scale the Ni-ZnO rods diameter were determined to be on average 60 nm.

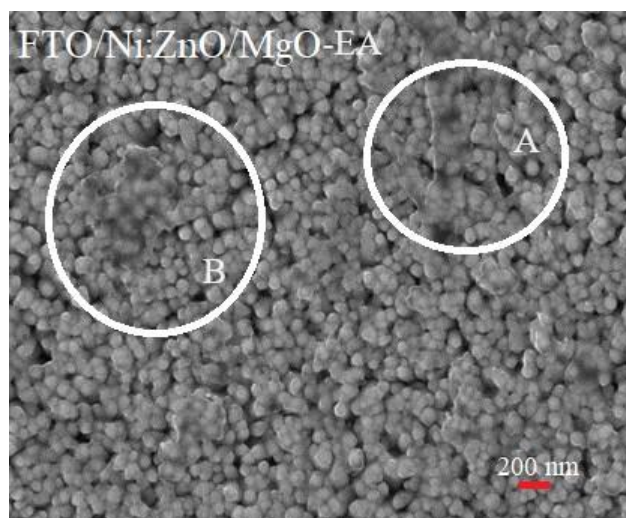


FIGURE 24: A SEM image for as prepared layer FTO/Ni-ZnO/MgO-EA

4.2.2 OPTICAL ANALYSIS

FIGURE 25 shows the transmittance and absorbance spectra of different devices of FTO/Ni-ZnO/MgO-EA treated with Rosebengal (RB) and Brilliant black burn (BBBN). From FIGURE 25 (a) it can be observed that the FTO/Ni-ZnO/MgO-EA sample presented higher transmittance within the visible wavelength region compared to dye treated samples.

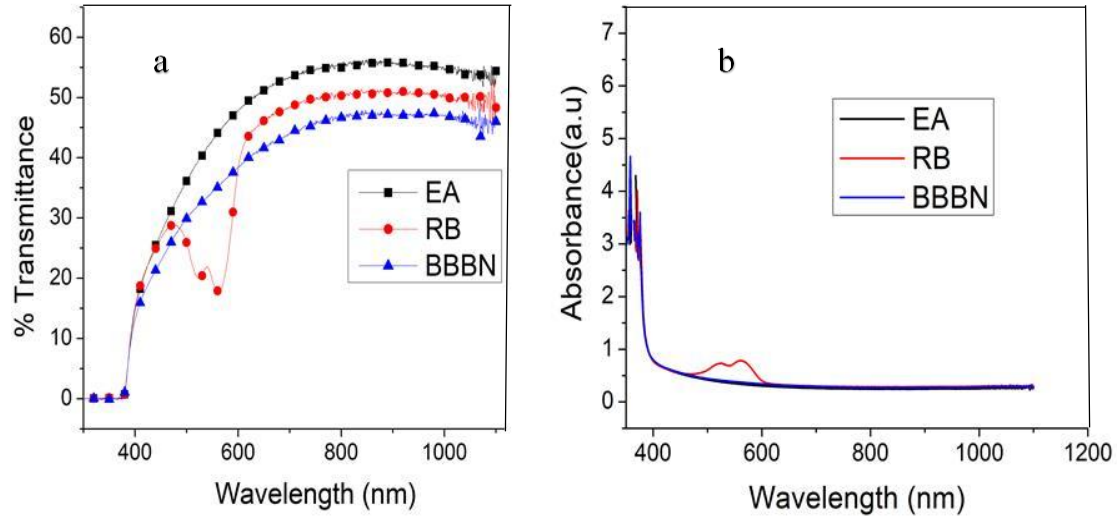


FIGURE 25: Optical transmittance (a) and absorbance (b) for different dye treatments RB and BBN

The RB treated layers presented a fall in transmittance in the region 475 nm to 580 nm. This drop in transmittance can be associated with the change in transition from ground state to excited state of the RB dye [103] [113]. However, the RB dye exhibit a higher transmittance in regions above 580 nm as compared to the BBN dye treated layers. These behaviour is further seen in the absorbance spectra (FIGURE 25 (b)) whereby the RB treated samples exhibit higher absorbance factor within the ranges of 475 nm to 580 nm meaning the lower transmittance is due to higher absorption. The bandgap values were determined using the Tauc method as depicted in FIGURE 26.

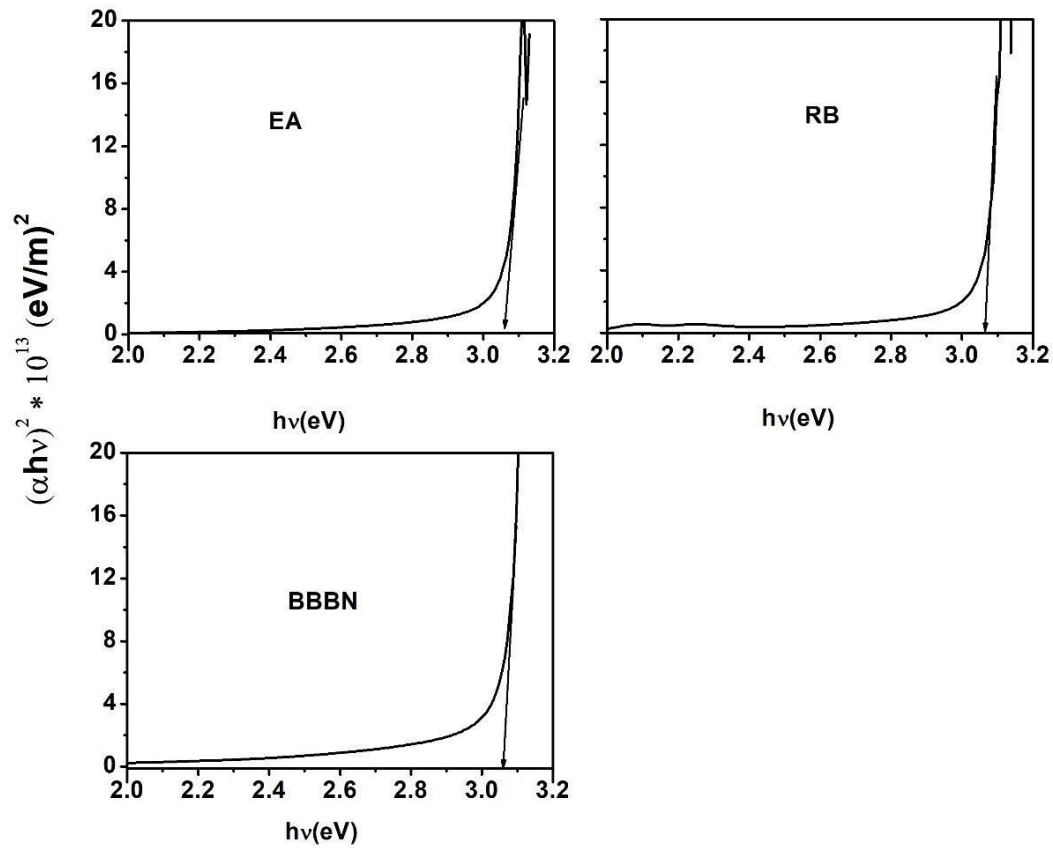


FIGURE 26: Graph showing band gap energies E_g for EA, RB, BBBN, treated FTO/Ni- ZnO/MgO-EA layers.

By plotting $(\alpha h\nu)^2$ against $h\nu$ from equation 6 and extrapolating the linear region of the band tail to the x intercept the bandgap values were determined. The obtained values are recorded in Table 4 below. The obtained values of bandgap are within the range of 3.05 eV to 3.06eV. This shows that the dye does not alter the band gap of the under-laying nanostructures as the difference of 0.01 eV was observed.

Table 5: Estimated band gap energies for EA, RB and BBBN treated samples

FTO/Ni-ZnO/MgO-EA	Band gap (eV)
EA	3.05
RB	3.06
BBBN	3.06

However, the bandgap values have remained around the acceptable ZnO range of bandgap energy values which is around 3.01 eV to 3.3 eV [114].

4.2.3 ELECTRICAL STUDIES

The obtained electrical properties of the dye treated FTO/Ni-ZnO/MgO-EA were obtained from the Hall effect machine and tabulated in Table 6. The lowest conductivity value of 9.92×10^2 ($1/\Omega\text{cm}$) was obtained through RB treatment while higher conductivity of 1.26×10^3 ($1/\Omega\text{cm}$) were obtained through treatment of BBBN. The increased conductivity obtained on the RB treated thin film can be correlated to high mobility values and optimally lower carrier concentrations in the order of $\sim 10^{19}$ - 10^{21} ($/\text{cm}^3$). At these carrier concentration values it is established that thermal conductivity is well minimized therefore allowing electrical conductivity to increase [115] [116].

Table 6: Electrical parameters of dye treated FTO/Ni:ZnO/MgO-EA

Sample	Bulk Concentration $\times 10^{20}$ ($/\text{cm}^3$)	Sheet Resistance ($\Omega/\square$)	Resistivity $\times 10^{-4}$ (Ωcm)	Conductivity $\times 10^3$ ($1/\Omega\text{cm}$)	Mobility (Cm / Vs)
EA	2.40	6.19	9.66	1.04	26.9
Rose Bengal	2.12	6.59	10.1	0.99	29.6
Blackburn BN	7.57	6.19	7.93	1.26	25.6

4.2.3.1 I-V characteristics of solar cells

Figure 27 shows a schematic representation of the fabricated solar cell. The measured Current –Voltage (I-V) characteristics were measured and their relationship is shown in FIGURE 27. FIGURE 28 (a) shows I-V characteristics of different layer treatments. It was observed that FTO/Ni-ZnO/MgO-EA treated with RB produced the highest open circuit voltage (V_{oc}) of 0.12 V followed by the untreated and BBBN with 0.089 V and 0.02 V respectively. It was observed that even though the RB increased voltage it traded off in short circuit current (I_{sc}) current

production properties as it produced the lowest current value of 0.134mA compared to EA and BBBN treatments. The highest short circuit

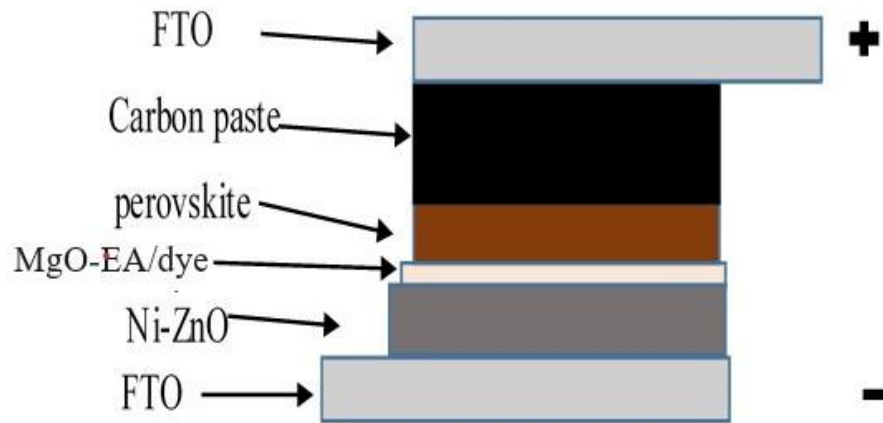


FIGURE 27: A schematic representation of the fabricate solar cell device.

current was observed with EA at 0.203 mA followed by BBBN at 0.193 mA. The V_{oc} and I_{sc} values are recorded in Table 7. These property altercations of current and voltage properties by dye treatments is an expected phenomenon. It is known that dyes exhibit a light harvesting ability that aid in photoelectron generation and electron transfers within the semiconducting material [117] [118]. The maximum power (P_{max}) produced by the individual solar cells was calculate as a product voltage and current according to equation 15,

$$P_{max} = V_{mp} * I_{mp} \dots\dots\dots 15$$

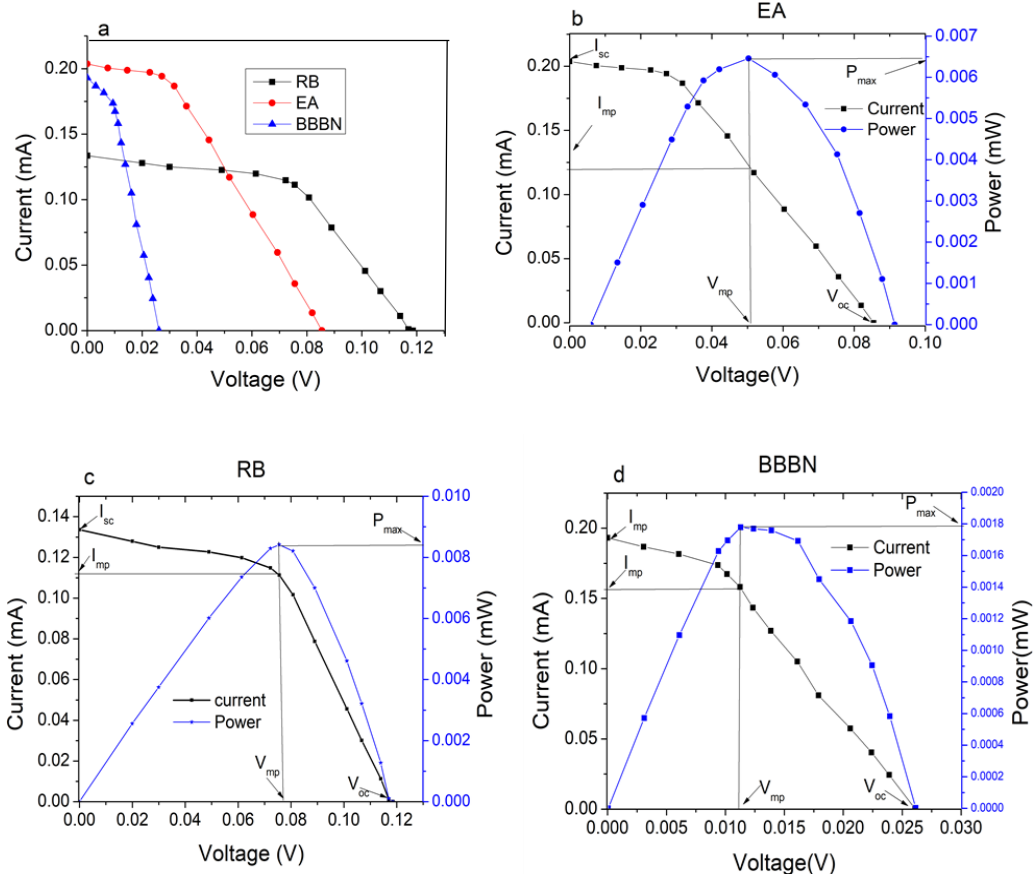


FIGURE 28: I-V characteristics for the fabricated solar cells (a) I-V curves for all fabricated samples (b) Ethanalamine treated sample (c) Rose Bengal treated sample (d) BlackBurn BN treated sample.

where V_{mp} and I_{mp} corresponds to maximum working voltage and current respectively. The values of V_{mp} were obtained by extrapolating the P_{max} peak all the way to the x-axis. And the values of I_{mp} were obtained by extrapolating to the y-axis the interception of V_{mp} line with the I-V curve [30] as shown in Figure 25 (b), (c) and (d). From the graphs it was observed that RB treated solar cell produced the maximum power of 0.0084 mW followed by EA and BBN with 0.00645 mW and 0.00179 mW respectively. Maximum power generated per active area of 1.5 cm² was calculated for each solar cell and the obtained values were recorded in Table 7.

Table 7: I-V parameters of the fabricated samples

	V_{oc}	I_{sc}	$V_{oc} * I_{sc}$	$V_{oc} * I_{sc}$	P_{max}	P_{max}	FF	n
	(V)	(mA)	(mW)	(mW/cm ²)	(mW)	(mW/cm ²)		%
EA	0.09	0.203	0.0027	0.0115	0.00645	0.00430	0.37	0.0043
RB	0.12	0.134	0.0161	0.0105	0.00840	0.00560	0.53	0.0056
BBBN	0.02	0.193	0.0039	0.0030	0.00179	0.00119	0.40	0.0012

The Fill Factor (FF) which is the ability of the solar cell to convert sunlight to electricity was calculated according as the ratio of P_{max} to $(V_{oc} * I_{sc})$. A high value of 0.53 FF was obtained using RB treatment followed by 0.40 for BBBN then 0.37 for EA treatment. Another parameter used to evaluate the performance of the solar cell is efficiency (n) which is the percentage ratio of the generated power to the solar radiation incident on the surface of the solar cell. In this research the solar radiation was 0.1 W/cm². The solar cell efficiency was calculated using equation 1 and the obtained values were recorded in Table 7. The highest efficiency of 0.0056% was obtained with RB treatment followed by the untreated (EA) and BBBN. [31] [32]. The higher performance of the RB treated device over the BBBN dye can be correlated to higher transmittance within the visible ranger spectrum which lowers the charge transfer resistance resulting in longer charge carrier lifetime compared to BBBN dye [119].

4.3 CONCLUSIONS AND RECOMMENDATIONS

4.3.1 CONCLUSIONS

Undoped and Ni_x-ZnO nano-rods thin films were synthesized through seed-assisted chemical bath deposition method. All samples showed a strong orientation toward a hexagonal wurtzite with a mix of zinc blende inclined to the (002) peak plane with no NiO secondary phase. This result was further confirmed by the Raman analysis spectroscopy which indicated prevalence of the 441 cm⁻¹ and 558 cm⁻¹ Raman mode shifts. Improved optical and electrical characteristics were observed upon Ni doping. The 2% sample showed higher transmittance in the visible spectrum, an acceptable band gap energy of average 3.12 eV, as well as low resistivity of $6 \times 10^{-4} \Omega\text{cm}$ compared to a higher value $3.5 \times 10^{-3} \Omega\text{cm}$ of the undoped Zinc Oxide sample. AFM micrographs showed that Low Ni dopant levels lead to smoother surface and triangulated grains. The obtained FOM was $22.71 \times 10^{-7} (\Omega)^{-1}$ and we therefore conclude that the 2% Nickel doped Zinc oxide can be a good dopant ratio for application in perovskite solar cells. The 2% Ni doped ZnO ETL was further modified with MgO-EA/Dye and its performance was evaluated in a solar cell. The Solar cell device was constructed with structure FTO/Ni- ZnO/MgO-EA/Dye/perovskite/Carbon/FTO in which RB and BBBN dyes were used. In general, the MgO-EA/dye modification led to reduction in the overall transmittance compared to MgO-EA thin film. The MgO-EA layer showed higher transmittance followed by RB treated and lastly BBBN dye treated layer. The SEM micrograph showed a clear layer of MgO having formed over the Ni-ZnO nanorods. The estimated band gap energies of the ETL were not altered following dye modifications as they were found to be within the acceptable ZnO band gap values of (3-3.3) eV. From these observations it can be suggested that for application in ETLs, dye treatments which do not significantly alter the optical properties of the ETL are to be considered. The RB treated device proved to be the highest performing cell as it showed high values of V_{oc} (0.12V), Power (0.00560 W/cm²), FF (0.53) and efficiency (0.0056). The BBBN treated layer produced low values of V_{oc} 0.02 V and high I_{sc} current of 0.193 mA leading to a lower overall performance compared to the untreated MgO-EA and RB treated devices. The MgO-EA treated cell produce high I_{sc} current of 0.203 mA and V_{oc} of 0.09 V however its overall performance was lower than RB treated cell. This can be understood through the FF parameter. From the observed values of FF for the three samples it can be concluded that dye treatments

lead to higher FF ratio hence an overall performance of the solar cell.

4.3.2 RECOMMENDATIONS

The impact of Ni doping and structural alterations through MgO-EA/Dye modification in this research has been undertaken. Nickel doping (Ni) is known to increase conductive, MgO-EA is known to increase stability while dyes are known to facilitate in electron transfer hence the combination in this research. The impact of doping, structural defects and of dyes on the ETL can be studied further to pursue the high efficiency of solar cells. Also to address the manufacturing costs, the replacement of HTLs with carbon based materials has been seen as right path to take and more studies can also be undertaken in this area.

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